

Liza M. Walsh
Christine I. Gannon
CONNELL FOLEY LLP
85 Livingston Avenue
Roseland, New Jersey 07068
Tel.: (973) 535-0500
Fax: (973) 535-9217

*Attorneys for Plaintiff
TransWeb, LLC*

**IN THE UNITED STATES DISTRICT COURT
FOR THE DISTRICT OF NEW JERSEY**

_____)	
TRANSWEB, LLC,)	CIVIL ACTION No. 10-04413 (FSH/PS)
)	
Plaintiff,)	
)	
v.)	AMENDED COMPLAINT
)	AND JURY DEMAND
3M INNOVATIVE PROPERTIES)	
COMPANY and 3M COMPANY,)	
)	
Defendants.)	
_____)	

Plaintiff TransWeb, LLC (“TransWeb”) hereby brings this action against Defendants 3M Innovative Properties Company and 3M Company (collectively “Defendants”), alleging as follows:

THE PARTIES

1. Plaintiff TransWeb, LLC, is a limited liability corporation organized and existing under the laws of the state of New Jersey with its principal place of business at 1473 West Forest Grove Road, Vineland, New Jersey, 08360.

2. Defendant 3M Innovative Properties Company is a corporation organized and existing under the laws of the state of Delaware with its principal place of business at 3M Center, St. Paul, Minnesota, 55133-3427.

3. Defendant 3M Company is a corporation organized and existing under the laws of the state of Delaware with its principal place of business at 3M Center, St. Paul, Minnesota, 55133-3427.

JURISDICTION AND VENUE

4. This action arises under the Declaratory Judgment Act, 28 U.S.C. §§ 2201, and the patent laws of the United States, 35 U.S.C. § 1 et seq.

5. This Court has subject matter jurisdiction over this action under at least 28 U.S.C. §§ 1331, 1338, 2201 and 2202.

6. Defendant 3M Innovative Properties Company is registered to do business in New Jersey with identification number 100783929, and has appointed as an agent for service of process in this judicial district The Corporation Trust Company, 820 Bear Tavern Road, West Trenton, New Jersey, 08628. 3M Innovative Properties Company has repeatedly availed itself of the forum provided by this judicial district. Most recently, 3M Innovative Properties Company is a plaintiff in the currently ongoing *Graceway Pharmaceuticals, LLC et al. v. Perrigo Company et al.*, Civil Action No. 10-937 (D.N.J.), filed on February 23, 2010.

7. Defendant 3M Company is registered to do business in New Jersey with identification number 6112410000, and has appointed as an agent for service of process in this judicial district The Corporation Trust Company, 820 Bear Tavern Road, West Trenton, New Jersey, 08628. 3M Company maintains multiple facilities in New Jersey, including in Parsippany, Flemington, and Belle Mead, New Jersey.

8. Upon information and belief, Defendants have continuous and systematic contacts in New Jersey, including maintaining offices and doing business in New Jersey, and are subject to the personal jurisdiction of this Court under the United States Constitution, the laws of the state of New Jersey, and the Federal Rules of Civil Procedure.

9. Venue is proper in this judicial district under 28 U.S.C. §§ 1391 and 1400(b).

FILTRATION METHODS AND TERMINOLOGY

10. Filtration is the removal of unwanted material from a stream of gas or liquid. Filtration “media” is the material that performs the filtration. When a gas or liquid moves through filtration media, the media filters it by allowing some material to pass, while blocking or retaining other material – the contaminants.

11. Filtration media can perform this function in several ways. Some filtration media perform purely “mechanical” filtration, in which the media’s pores are large enough to allow desirable matter through, but small enough to block contaminants. For example, a coffee filter performs mechanical filtration: the brewed coffee passes through the filter, while the larger coffee grounds are prevented from passing.

12. In addition to mechanical filtration, some filtration media also use chemical or electric attraction to filter contaminants. For example, an “electrostatically charged” air filter will attract contaminant particles carrying an opposite charge, causing them to stick to the media even if they might otherwise be small enough to pass through.

13. Similarly, depending on its source material and fabrication technique, filtration media may have innate chemical properties that attract or repel certain contaminant particles. For example, material that is “hydrophilic,” or water-loving, may attract and hold water molecules while letting other molecules pass through.

14. A filter's "efficiency" describes its ability to remove a contaminant, in percentage terms. If a filter is rated with a 75% efficiency regarding a particular contaminant, it will remove 75% of that contaminant, either by weight or by volume, under lab conditions. Generally speaking, the more "efficient" filter media is, the better job it does filtering out contaminants.

15. Because any filter interferes, at least somewhat, with the flow of gas or liquid through it, the pressure on the outflow side will generally be lower than the pressure on the inflow side, reflecting the force necessary to push the gas or liquid through the filter. In air filtration, this differential is known as "pressure drop," which measures the difference in air pressure between the filter's inflow and outflow sides.

16. Filtration media with a low pressure drop requires less energy to move air through the filter than filtration media with a high pressure drop. Consequently, a person wearing a respirator with low-pressure-drop media can breathe more easily and in a less restricted fashion than a person wearing a respirator with high-pressure-drop media. As a result, air filtration media with a low pressure drop is more desirable than media with a high pressure drop.

17. Makers of filtration media often face a trade-off between efficiency and pressure drop. In order to remove more contaminants and therefore achieve a higher efficiency, filtration media generally must restrict more air flow and therefore suffer from a higher pressure drop. Manufacturers strive to develop filtration media that has both high efficiency and low pressure drop.

18. This trade-off between efficiency and pressure drop is most apparent in filtration media relying solely on mechanical filtration. Mechanical filtration requires forcing a gas through pores small enough to block contaminants (*supra* ¶ 11); smaller pores mean greater efficiency, but require more energy to pass material through them, especially as they clog up

with contaminants. For this reason, manufacturers of filtration media often use additional materials and techniques, such as electrostatically charged media, to improve efficiency without overly increasing pressure drop.

TRANSWEB'S INVENTION AND PATENT APPLICATION

19. Beginning in the fall of 1996, TransWeb worked to develop an electrostatically charged air filtration media that had both high efficiency and low pressure drop.

20. Prior to 1996, 3M had manufactured electrostatically charged filtration media using a process of infusing the media with chemicals containing fluorine, the best element for imparting an electrical charge. In other words, 3M used fluorine as an ingredient in the media's fibers themselves.

21. During its development efforts, TransWeb discovered that it could produce filtration media with both high efficiency and low pressure drop by "surface-treating" media with a fluorine-rich plasma, rather than infusing the fibers themselves with chemicals containing fluorine. TransWeb's surface-treated filtration media performed comparably to 3M's filtration media infused with fluorine, and could be produced at a lower price.

22. TransWeb's filtration media surface-treated with a fluorine-rich plasma was also more "hydrophobic" and "oleophobic" than filtration media infused with chemicals containing fluorine – that is, it was better at repelling both water and oil. Increased hydrophobicity and oleophobicity are desirable features for filtration media used in environments with water or oil in the air, such as a respirator used in a paint booth. In general terms, hydrophobic and oleophobic filtration media cause water and oil molecules to bead on the media's surface, rather than spread across it, and will therefore hold more of these molecules, improving the life of the filter.

23. On April 30, 1997, TransWeb filed U.S. patent application no. 08/841,348, describing a "filter medium, comprising a web of electret fibers, said fibers having been formed

from a material that was treated with a fluorine-containing plasma prior to being electrically charged.”

24. On January 28, 1998, the examiner’s first office action rejected all claims of the ’348 application, stating that “it would have been readily obvious to one having ordinary skill in the art to apply a fluorine additive by plasma treatment to the admitted prior art fibrous filter element and method of production in order to enhance the separation properties of the filter element.”

25. On April 27, 1998, Transweb amended the ’348 application.

26. On July 15, 1998, the examiner issued a final rejection of all claims in the ’348 application. TransWeb did not further pursue the ’348 application, leading to its abandonment.

TRANSWEB’S MARKETING OF ITS INVENTION

27. At least as early as December 1996, TransWeb began meeting with potential customers of its new product. On December 17, 1996, TransWeb met with representatives of Racal Filter Technologies, Inc. (“Racal”). Following this meeting, TransWeb sent Racal samples of its new filtration media on December 21, 1996.

28. Racal and TransWeb representatives met again in late April or early May 1997. During these meetings, TransWeb offered to sell Racal its new filtration media surface-treated with a fluorine-rich plasma. Following further discussions, TransWeb shipped another set of samples to Racal on May 7, 1997.

29. After TransWeb filed the ’348 application, in May 1997, TransWeb informed Racal that it had applied for a patent covering its new filtration media surface-treated with a fluorine-rich plasma.

3M'S ACQUISITION OF RACAL AND ANALYSIS OF TRANSWEB'S INVENTION

30. In December 1997, 3M agreed to purchase the assets of Racal. In early 1998, no later than March 31, 1998, 3M closed the transaction and acquired Racal's assets. Among these assets were at least some of the samples TransWeb sent to Racal in 1996 and 1997. (*Supra* ¶¶ 27-28.) On information and belief, these assets included all of the samples TransWeb sent to Racal in 1996 and 1997, records regarding meetings between TransWeb and Racal during which TransWeb informed Racal of its patent application covering its filtration media surface-treated with a fluorine-rich plasma and offered to sell Racal this media, and employees who attended such meetings.

31. 3M analyzed TransWeb's samples provided to Racal.

32. On December 2, 1998, 3M's "Corporate Research Laboratories, Corporate Analytical Technology Center, Surface Analysis" reported detailed results regarding 3M's analysis of TransWeb's samples provided to Racal. According to the report from 3M's Corporate Research Laboratories, it undertook this analysis because "Dr. J. S. Huberty, Occupational Health & Environmental Safety Division, submitted a sample of the non-woven web labeled Transweb T-Melt 30P. He requested that the chemical composition of the surface of the sample be determined, especially to determine the amount of fluorine present." 3M's Corporate Research Laboratories reported that approximately 50% of the surface molecules were fluorine, with the balance comprising carbon, oxygen, and nitrogen. 3M's Corporate Research Laboratories also reported that the samples indicated "exposure to a high energy plasma or corona type treatment."

3M'S PURCHASE OF TRANSWEB FILTRATION MEDIA

33. Beginning in 1999, 3M inquired with TransWeb regarding 3M's desire to purchase from TransWeb filtration media surface-treated with a fluorine-rich plasma.

34. In June, July and August 2000, TransWeb shipped to 3M filtration media surface-treated with a fluorine-rich plasma in non-commercial quantities, which 3M told TransWeb it would use for evaluation and experimentation.

35. From April through July 2001, and again from May through September 2002, TransWeb sold and shipped to 3M commercial quantities of filtration media surface-treated with a fluorine-rich plasma.

PROSECUTION OF THE '458 PATENT

36. On January 6, 2000, at least two-and-a-half years after TransWeb provided Racal with filtration media surface-treated with a fluorine-rich plasma and approximately two years after 3M purchased Racal's assets, including TransWeb's media, 3M filed application no. 09/478,658, which would eventually become the '458 patent.

37. 3M's filing of the '658 application triggered the legal duty of candor to the patent office, including disclosure of information material to patentability. "Each individual associated with the filing and prosecution of a patent application has a duty of candor and good faith in dealing with the Office, which includes a duty to disclose to the Office all information known to that individual to be material to patentability as defined in this section. The duty to disclose information exists with respect to each pending claim until the claim is cancelled or withdrawn from consideration, or the application becomes abandoned." 37 C.F.R. § 1.56(a) (July 1, 1999); Manual of Patent Examining Procedure § 2001 (7th ed. July 1998). Applicants before the patent office had a duty to disclose "all information known to that individual to be material to patentability" *promptly*, generally before the first office action by the Patent and Trademark Office. 37 C.F.R. § 1.59 (July 1, 1999).

38. Despite this duty, neither 3M nor any other individual associated with the filing and prosecution of the '658 application disclosed any information regarding TransWeb's

filtration media surface-treated with a fluorine-rich plasma, which 3M had in its possession since early 1998, and had analyzed in December 1998.

39. 3M and other individuals associated with the filing and prosecution of the '658 application violated this duty by failing to disclose TransWeb's filtration media surface-treated with a fluorine-rich plasma, which was anticipatory prior art to the '658 application.

40. 3M and other individuals associated with the filing and prosecution of the '658 application knew, from 3M's acquisition of Racal's assets, that TransWeb had offered to sell Racal its filtration media surface-treated with a fluorine-rich plasma no later than May 1997, more than a year before the claimed priority date of the '658 application.

41. 3M and other individuals associated with the filing and prosecution of the '658 application knew, from 3M's acquisition of Racal's assets, that TransWeb had informed Racal in May 1997 that it had applied for a patent covering its new filtration media surface-treated with a fluorine-rich plasma.

42. 3M and other individuals associated with the filing and prosecution of the '658 application knew, from 3M's analysis of the TransWeb samples in December 1998, that TransWeb's filtration media surface-treated with a fluorine-rich plasma was material to patentability of the '658 application.

43. For example, claim 25 of the '658 application claimed a "method of making an electret comprising: fluorinating a polymeric nonwoven web to produce an article having surface fluorination; and charging the fluorinated web in a manner sufficient to produce an electret."

44. As 3M's own "Corporate Research Laboratories" report had confirmed in December 1998, each limitation of this claim was already present in TransWeb's filtration media

surface-treated with a fluorine-rich plasma. (*Supra* ¶ 32.) The report confirmed that TransWeb's product was a "non-woven web" with significant surface fluorination that had been subject to "exposure to a high energy plasma or corona type treatment."

45. Despite its clear materiality to patentability of the '658 application, neither 3M nor any other individual associated with the filing and prosecution of the '658 application disclosed TransWeb's filtration media surface-treated with a fluorine-rich plasma to the Patent and Trademark Office for *almost two years*, until December 11, 2001. A true and correct copy of this disclosure is attached as Exhibit A.

46. 3M and the other individuals associated with the filing and prosecution of the '658 application withheld information from the Patent and Trademark Office with the deceptive intent of preventing the Patent and Trademark Office from realizing that TransWeb's media was anticipatory prior art to the '658 application.

47. When 3M did disclose TransWeb's filtration media surface-treated with a fluorine-rich plasma to the Patent and Trademark Office, it did so in a deceptive and misleading fashion. For example, 3M's December 2001 disclosure stated that, "[o]n June 2, 1997, Racal Filter Technologies, Inc, (Racal) entered into a Confidential Disclosure Agreement (Exhibit A) with Transweb, LLC. As part of this arrangement between the parties, Transweb furnished to Racal a sample of a nonwoven filtration web."

48. This was not correct: TransWeb sent Racal samples in December 1996 and May 1997, and did not execute the Confidential Disclosure Agreement until June 2, 1997. (*Supra* ¶¶ 27-28; Exhibit A.)

49. Neither 3M nor any other individual associated with the filing and prosecution of the '658 application disclosed that TransWeb sent its filtration media surface-treated with a

fluorine-rich plasma to Racal without executing any non-disclosure agreement, that is, without any restriction on Racal's redistribution.

50. This information was material to the patentability of the '658 application. If TransWeb sent its filtration media surface-treated with a fluorine-rich plasma to Racal without executing any non-disclosure agreement, that is, without any restriction on Racal's redistribution, then TransWeb's media was "in public use or on sale in this country, more than one year prior to the date of the application for patent in the United States," and therefore could be anticipatory prior art to the '658 application. 35 U.S.C. § 102(b).

51. 3M and the other individuals associated with the filing and prosecution of the '658 application withheld information from the Patent and Trademark Office with the deceptive intent of preventing the Patent and Trademark Office from realizing that TransWeb's media was "in public use or on sale in this country, more than one year prior to the date of the application for patent in the United States," and therefore could be anticipatory prior art to the '658 application. 35 U.S.C. § 102(b).

52. 3M's December 2001 disclosure further stated that, "[t]he applicants are unaware of any public disclosure of the Tmelt 30P product before the July 2, 1998 filing date." Again, this was not correct. TransWeb sent Racal samples in December 1996 and May 1997, and did not execute the Confidential Disclosure Agreement until June 2, 1997. (*Supra* ¶¶ 27-28; Exhibit A.)

53. Neither 3M nor any other individual associated with the filing and prosecution of the '658 application disclosed that TransWeb sent its filtration media surface-treated with a fluorine-rich plasma to Racal without executing any non-disclosure agreement, that is, without any restriction on Racal's redistribution.

54. This information was material to the patentability of the '658 application. If TransWeb sent its filtration media surface-treated with a fluorine-rich plasma to Racal without executing any non-disclosure agreement, that is, without any restriction on Racal's redistribution, then TransWeb's media was "in public use or on sale in this country, more than one year prior to the date of the application for patent in the United States," and therefore could be anticipatory prior art to the '658 application. 35 U.S.C. § 102(b).

55. 3M and the other individuals associated with the filing and prosecution of the '658 application withheld information from the Patent and Trademark Office with the deceptive intent of preventing the Patent and Trademark Office from realizing that TransWeb's media was "in public use or on sale in this country, more than one year prior to the date of the application for patent in the United States," and therefore could be anticipatory prior art to the '658 application. 35 U.S.C. § 102(b).

56. 3M's December 2001 disclosure further stated that, "[a]s part of the purchase of Racal's assets, 3M obtained possession of the Transweb product that was submitted under the Confidential Disclosure Agreement dated June 2, 1997." Again, this was not correct. TransWeb sent Racal samples in December 1996 and May 1997, and did not execute the Confidential Disclosure Agreement until June 2, 1997. (*Supra* ¶¶ 27-28; Exhibit A.)

57. Neither 3M nor any other individual associated with the filing and prosecution of the '658 application disclosed that TransWeb sent its filtration media surface-treated with a fluorine-rich plasma to Racal without executing any non-disclosure agreement, that is, without any restriction on Racal's redistribution.

58. This information was material to the patentability of the '658 application. If TransWeb sent its filtration media surface-treated with a fluorine-rich plasma to Racal without

executing any non-disclosure agreement, that is, without any restriction on Racal's redistribution, then TransWeb's media was "in public use or on sale in this country, more than one year prior to the date of the application for patent in the United States," and therefore could be anticipatory prior art to the '658 application. 35 U.S.C. § 102(b).

59. 3M and the other individuals associated with the filing and prosecution of the '658 application withheld information from the Patent and Trademark Office with the deceptive intent of preventing the Patent and Trademark Office from realizing that TransWeb's media was "in public use or on sale in this country, more than one year prior to the date of the application for patent in the United States," and therefore could be anticipatory prior art to the '658 application. 35 U.S.C. § 102(b).

60. 3M's December 2001 disclosure further stated that, "[a]pplicants do believe, however, that the product may have been subsequently commercialized by Transweb." Once again, this was not correct. By the time 3M filed its disclosure in December 2001, TransWeb had sold and shipped to 3M filtration media surface-treated with a fluorine-rich plasma in commercial quantities. (*Supra* ¶ 35.) 3M knew that TransWeb had actually commercialized its filtration media surface-treated with a fluorine-rich plasma as early as April 2001, when it began to purchase commercial quantities of this media; 3M could not truly state that "the product *may* have been subsequently commercialized by Transweb." (Emphasis added.)

61. Neither 3M nor any other individual associated with the filing and prosecution of the '658 application disclosed that TransWeb had actually commercialized its filtration media surface-treated with a fluorine-rich plasma as early as April 2001.

62. This information was material to the patentability of the '658 application. If TransWeb commercialized its filtration media surface-treated with a fluorine-rich plasma as

early as April 2001, it likely invented the media much earlier, and likely placed its media “in public use or on sale in this country, more than one year prior to the date of the application for patent in the United States,” which could therefore be anticipatory prior art to the ’658 application. 35 U.S.C. § 102(b).

63. 3M and the other individuals associated with the filing and prosecution of the ’658 application withheld information from the Patent and Trademark Office with the deceptive intent of preventing the Patent and Trademark Office from realizing that TransWeb’s media was “in public use or on sale in this country, more than one year prior to the date of the application for patent in the United States,” and therefore could be anticipatory prior art to the ’658 application. 35 U.S.C. § 102(b).

64. Finally, 3M’s December 2001 disclosure stated that “[n]o patent applications are believed to have been filed by Transweb for this product.” Once again, this was not correct. 3M and other individuals associated with the filing and prosecution of the ’658 application knew, from 3M’s acquisition of Racal’s assets, that TransWeb had informed Racal in May 1997 that it had applied for a patent covering its new filtration media surface-treated with a fluorine-rich plasma. (*Supra* ¶ 29.)

65. Neither 3M nor any other individual associated with the filing and prosecution of the ’658 application disclosed that TransWeb had informed Racal in May 1997 that it had applied for a patent covering its new filtration media surface-treated with a fluorine-rich plasma.

66. This information was material to the patentability of the ’658 application. If TransWeb had applied for a patent covering its new filtration media surface-treated with a fluorine-rich plasma before May 1997, when it informed Racal of its existing application, its invention clearly occurred before 3M’s alleged invention underlying the ’658 application.

67. 3M and the other individuals associated with the filing and prosecution of the '658 application withheld information from the Patent and Trademark Office with the deceptive intent of preventing the Patent and Trademark Office from realizing that TransWeb invented its media, and filed for a patent, more than two-and-a-half years before 3M filed the '658 application.

68. On June 4, 2002, the United States Patent and Trademark Office issued U.S. Patent No. 6,397,458 ("the '458 Patent"). A true and correct copy of the '458 Patent is attached as Exhibit B. On information and belief, 3M Innovative Properties Company is the owner by assignment of all right, title and interest in the '458 Patent, and 3M Company is the exclusive licensee of the '458 Patent.

69. During prosecution of the '458 Patent, Defendants, the named inventors, and other individuals associated with the prosecution of the '458 Patent failed to cite material prior art information, publications and other material showing, among other things, the availability of anticipating technology more than one year prior to the priority date of the '458 Patent. Defendants, the named inventors, and other individuals associated with the prosecution of the '458 Patent withheld this prior art information, publications and other material from the Patent and Trademark Office with deceptive intent. To the extent Defendants, the named inventors, and other individuals associated with the prosecution of the '458 Patent did provide some information regarding this material prior art, they did so in a deceptive fashion intended to conceal critical elements of the information that would, if known to the Patent and Trademark Office, cause the Patent and Trademark Office to deny issuance of the '458 Patent. As a result, the inventors obtained the '458 Patent by knowingly and willfully misrepresenting facts to the Patent and Trademark Office.

PROSECUTION OF THE '551 PATENT

70. On October 7, 2003, 3M filed application no. 10/681,670, which would eventually become the '551 patent.

71. 3M's filing of the '670 application triggered the legal duty of candor to the patent office, including disclosure of information material to patentability. "Each individual associated with the filing and prosecution of a patent application has a duty of candor and good faith in dealing with the Office, which includes a duty to disclose to the Office all information known to that individual to be material to patentability as defined in this section. The duty to disclose information exists with respect to each pending claim until the claim is cancelled or withdrawn from consideration, or the application becomes abandoned." 37 C.F.R. § 1.56(a) (July 1, 2003); Manual of Patent Examining Procedure § 2001 (8th ed. rev. 1 Feb. 2003).

72. 3M and other individuals associated with the filing and prosecution of the '670 application knew, from 3M's analysis of the TransWeb samples in December 1998, that TransWeb's filtration media surface-treated with a fluorine-rich plasma was material to patentability of the '670 application.

73. Indeed, 3M and other individuals associated with the filing and prosecution of the '670 application admitted that TransWeb's filtration media surface-treated with a fluorine-rich plasma was material to patentability of the '670 application by disclosing it in their first Invention Disclosure Statement filed in the '670 application. (Exhibit C.)

74. Although 3M did disclose TransWeb's filtration media surface-treated with a fluorine-rich plasma to the Patent and Trademark Office, it did so in a deceptive and misleading fashion. The disclosure related to TransWeb's filtration media surface-treated with a fluorine-rich plasma in the '670 application is identical to the disclosure in the '658 application (*compare*

Exhibit A *with* Exhibit C), and the deceptive aspects of the disclosure are therefore also identical. (*Supra* ¶¶ 47-67.)

75. On October 26, 2004, the United States Patent and Trademark Office issued U.S. Patent No. 6,808,551 (“the ’551 Patent”). A true and correct copy of the ’551 Patent is attached as Exhibit D. On information and belief, 3M Innovative Properties Company is the owner by assignment of all right, title and interest in the ’551 Patent, and 3M Company is the exclusive licensee of the ’551 Patent.

76. During prosecution of the ’551 Patent, Defendants, the named inventors, and other individuals associated with the prosecution of the ’551 Patent failed to cite material prior art information, publications and other material showing, among other things, the availability of anticipating technology more than one year prior to the priority date of the ’551 Patent. Defendants, the named inventors, and other individuals associated with the prosecution of the ’551 Patent withheld this prior art information, publications and other material from the Patent and Trademark Office with deceptive intent. To the extent Defendants, the named inventors, and other individuals associated with the prosecution of the ’551 Patent did provide some information regarding this material prior art, they did so in a deceptive fashion intended to conceal critical elements of the information that would, if known to the Patent and Trademark Office, cause the Patent and Trademark Office to deny issuance of the ’551 Patent. As a result, the inventors obtained the ’551 Patent by knowingly and willfully misrepresenting facts to the Patent and Trademark Office.

THE MINNESOTA ACTION

77. On May 21, 2010, Defendants filed an action against TransWeb in the United States District Court for the District of Minnesota, captioned *3M Innovative Properties Company*

and 3M Company, v. TransWeb L.L.C., Civil Action No. 10-2132 (D. Minn.) (the “Minnesota Action”).

78. In the Minnesota Action, Defendants alleged that TransWeb directly infringed the ’458 Patent and the ’551 Patent (collectively, the “3M Asserted Patents”).

79. On July 2, 2010, Defendants served TransWeb with their Complaint in the Minnesota Action.

80. TransWeb does not have sufficient contacts with the State of Minnesota, and is therefore not subject to personal jurisdiction before the United States District Court for the District of Minnesota. For this reason, on August 20, 2010, TransWeb filed a timely motion to dismiss the Minnesota Action for lack of personal jurisdiction. The United States District Court for the District of Minnesota set this motion for hearing on October 20, 2010.

81. On September 29, 2010, 3M voluntarily dismissed the Minnesota action under Fed. R. Civ. P. 41(a)(1)(A)(i).

82. Although filed in a jurisdiction that cannot exercise personal jurisdiction over TransWeb, the Minnesota Action demonstrated an immediate, real, and justiciable controversy between TransWeb and Defendants over the validity and enforceability of the 3M Asserted Patents, and over TransWeb’s alleged infringement of the 3M Asserted Patents.

FIRST CAUSE OF ACTION
(Declaratory Judgment of Invalidity of the ’458 Patent)

83. TransWeb incorporates by reference the allegations set forth in paragraphs 1-82 of this Complaint.

84. The claims of the ’458 Patent are invalid under Title 35 of the United States Code, including but not limited to 35 U.S.C. §§ 101, 102, 103, 112, 200 *et seq.*, and 301 *et seq.*

85. An immediate, real, and justiciable controversy exists between TransWeb and Defendants regarding the validity of the '458 Patent.

86. TransWeb seeks a judgment declaring that the claims of the '458 Patent are invalid.

SECOND CAUSE OF ACTION
(Declaratory Judgment of Invalidity of the '551 Patent)

87. TransWeb incorporates by reference the allegations set forth in paragraphs 1-86 of this Complaint.

88. The claims of the '551 Patent are invalid under Title 35 of the United States Code, including but not limited to 35 U.S.C. §§ 101, 102, 103, 112, 200 *et seq.*, and 301 *et seq.*

89. An immediate, real, and justiciable controversy exists between TransWeb and Defendants regarding the validity of the '551 Patent.

90. TransWeb seeks a judgment declaring that the claims of the '551 Patent are invalid.

THIRD CAUSE OF ACTION
(Declaratory Judgment of Unenforceability for Inequitable Conduct of the '458 Patent)

91. TransWeb incorporates by reference the allegations set forth in paragraphs 1-90 of this Complaint.

92. Specifically, TransWeb incorporates by reference the allegations set forth in paragraphs 36-69 above.

93. An immediate, real, and justiciable controversy exists between TransWeb and Defendants regarding the enforceability of the '458 Patent.

94. TransWeb seeks a judgment declaring that the claims of the '458 Patent are unenforceable under the doctrine of inequitable conduct.

FOURTH CAUSE OF ACTION

(Declaratory Judgment of Unenforceability for Inequitable Conduct of the '551 Patent)

95. TransWeb incorporates by reference the allegations set forth in paragraphs 1-94 of this Complaint.

96. Specifically, TransWeb incorporates by reference the allegations set forth in paragraphs 70-76 above.

97. An immediate, real, and justiciable controversy exists between TransWeb and Defendants regarding the enforceability of the '551 Patent.

98. TransWeb seeks a judgment declaring that the claims of the '551 Patent are unenforceable under the doctrine of inequitable conduct.

FIFTH CAUSE OF ACTION

(Declaratory Judgment of Unenforceability for Laches of the '458 Patent)

99. TransWeb incorporates by reference the allegations set forth in paragraphs 1-98 of this Complaint.

100. Specifically, TransWeb incorporates by reference the allegations set forth in paragraphs 33-35 above.

101. An immediate, real, and justiciable controversy exists between TransWeb and Defendants regarding the enforceability of the '458 Patent.

102. TransWeb seeks a judgment declaring that the claims of the '458 Patent are unenforceable under the doctrine of laches.

SIXTH CAUSE OF ACTION

(Declaratory Judgment of Unenforceability for Laches of the '551 Patent)

103. TransWeb incorporates by reference the allegations set forth in paragraphs 1-102 of this Complaint.

104. Specifically, TransWeb incorporates by reference the allegations set forth in paragraphs 33-35 above.

105. An immediate, real, and justiciable controversy exists between TransWeb and Defendants regarding the enforceability of the '551 Patent.

106. TransWeb seeks a judgment declaring that the claims of the '551 Patent are unenforceable under the doctrine of laches.

SEVENTH CAUSE OF ACTION

(Declaratory Judgment of Non-infringement of the '458 Patent)

107. TransWeb incorporates by reference the allegations set forth in paragraphs 1-106 of this Complaint.

108. TransWeb has not infringed and does not infringe, directly or indirectly, any valid and enforceable claim of the '458 Patent.

109. An immediate, real, and justiciable controversy exists between TransWeb and Defendants regarding TransWeb's alleged infringement of the '458 Patent.

110. TransWeb seeks a judgment declaring that it does not infringe any claim of the '458 Patent.

EIGHTH CAUSE OF ACTION
(Declaratory Judgment of Non-infringement of the '551 Patent)

111. TransWeb incorporates by reference the allegations set forth in paragraphs 1-110 of this Complaint.

112. TransWeb has not infringed and does not infringe, directly or indirectly, any valid and enforceable claim of the '551 Patent.

113. An immediate, real, and justiciable controversy exists between TransWeb and Defendants regarding TransWeb's alleged infringement of the '551 Patent.

114. TransWeb seeks a judgment declaring that it does not infringe any claim of the '551 Patent.

PRAYER FOR RELIEF

WHEREFORE, TransWeb prays for judgment and relief as follows:

- A. Declaring that the '458 Patent and the '551 Patent are invalid;
 - B. Declaring that the '458 Patent and the '551 Patent are unenforceable;
 - C. Declaring that TransWeb does not infringe the '458 Patent or the '551 Patent;
 - D. Declaring that Defendants are not entitled to damages for or injunctive relief against any alleged infringement by TransWeb of the '458 Patent or the '551 Patent;
 - E. Finding that this is an exceptional case under 35 U.S.C. § 285;
 - F. Awarding TransWeb its costs and attorneys' fees in connection with this action;
- and
- G. Such further and additional relief as the Court deems just and proper.

DEMAND FOR JURY TRIAL

115. TransWeb demands a jury trial on all matters so triable.

Dated: November 12, 2010

CONNELL FOLEY LLP

By: s/ Liza M. Walsh

Liza M. Walsh
Christine I. Gannon
85 Livingston Avenue
Roseland, New Jersey 07068
(973) 535-0500
(973) 535-9217 facsimile
Attorneys for Plaintiff
TransWeb, LLC

Of Counsel:

QUINN EMANUEL URQUHART & SULLIVAN, LLP

Harold A. Barza *(to be admitted pro hac vice)*

Michael E. Williams *(to be admitted pro hac vice)*

Matthew Warren *(to be admitted pro hac vice)*

865 S. Figueroa Street

Los Angeles, California 90017

CERTIFICATION PURSUANT TO LOCAL CIVIL RULE 11.2

I hereby certify that the matter in controversy is not the subject of any other action pending in any court, or of any pending arbitration or administrative proceeding.

Dated: November 12, 2010

s/ Liza M. Walsh
Liza M. Walsh

CERTIFICATION PURSUANT TO LOCAL CIVIL RULE 201.1

I hereby certify that the above-captioned matter is not subject to compulsory arbitration in that the plaintiff seeks declaratory relief.

Dated: November 12, 2010

s/ Liza M. Walsh
Liza M. Walsh

EXHIBIT A

Patent
Docket No: 53205US013

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of:

MARVIN E. JONES ET AL.

Group Art Unit: 3729

Serial No.: 09/478,658

Filed: January 6, 2000

Examiner: Carl J. Arbes

For: METHOD OF MAKING AN ELECTRET ARTICLE BY TRANSFERRING FLUORINE TO THE
ARTICLE FROM A GASEOUS PHASE

SUPPLEMENTAL INFORMATION DISCLOSURE STATEMENT
PROPRIETARY MATERIAL

Assistant Commissioner for Patents
Washington, D.C. 20231

Dear Sir:

On June 2, 1997, Racal Filter Technologies, Inc. (Racal) entered into a Confidential Disclosure Agreement (Exhibit A) with Transweb, LLC. As part of this arrangement between the parties, Transweb furnished to Racal a sample of a nonwoven filtration web. The web was accompanied by a product sheet that outlined the filtration properties of a product designated as Tmelt 30P (Exhibit B).

In early 1998, 3M acquired the assets of Racal. As part of the purchase of Racal's assets, 3M obtained possession of the Transweb product that was submitted under the Confidential Disclosure Agreement dated June 2, 1997. This product was subsequently analyzed by 3M's corporate research laboratories, and a report was prepared, dated December 2, 1998. The product that was received from Transweb contained polymeric fibers, which were believed to be microfibers. The surface fluorination on the product was analyzed, and the results of the analysis are set forth in the 3M internal report dated December 2, 1998. Based on the inventors' review of the data set forth in the report, it is believed that the Transweb product had a $\text{CF}_3:\text{CF}_2$ ratio of at least 0.45, and possibly greater than 0.9. The quality factor for this product is believed to be somewhere between 0.13 and 0.62, based on the data supplied in the Transweb product sheet. The basis weight for the product was determined to be 30 g/m^2 .

USSN: 09/478,658

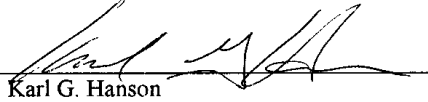
Docket No.: 53205US013

Although 3M acquired Racal prior to the filing date of the present application, neither the Transweb Tmelt 30P product, nor the product sheet, was shown or otherwise known to the inventors named in this patent application, or the undersigned, before the July 2, 1998 filing date of this patent application. The product is no longer in 3M's possession. It was returned to Transweb along with a letter dated April 28, 1999 (Exhibit C). The applicants are unaware of any public disclosure of the Tmelt 30P product before the July 2, 1998 filing date. Applicants do believe, however, that the product may have been subsequently commercialized by Transweb. No patent applications are believed to have been filed by Transweb for this product.

Registration Number	Telephone Number
32,900	651-736-7776
Date December 11, 2001	

Respectfully submitted,

By


Karl G. Hanson

Office of Intellectual Property Counsel
3M Innovative Properties Company
P.O. Box 33427
St. Paul, Minnesota 55133-3427
Facsimile: (651) 736-3833

BEST COPY



CONFIDENTIAL
Non-Disclosure Agreement

TransWeb, LLC
1473 West Forest Grove Rd.
Vineland, New Jersey 08360
Telephone 609-205-1313
Facsimile 609-205-1333

This Agreement is made this 24 of June, 1997
between TransWeb, LLC, herein referred to as "TransWeb" and
BAUER FILM TECHNOLOGIES, INC., herein
referred to as "The Undersigned".

This Agreement entails any and all matters seen, heard, or
learned during any visit to and/or communications with TransWeb.

The Undersigned acknowledges that in its course of dealings with
TransWeb, the Undersigned will receive specialized knowledge which, if
used in competition with TransWeb, could cause serious harm to
TransWeb.

In consideration of trade secret information provided by
TransWeb to the Undersigned and secret information provided to the
Undersigned by TransWeb, for various business purposes, the parties
agree:-

1. The Undersigned shall not communicate to any third party,
directly or indirectly, any confidential information received from
TransWeb, whether written or otherwise regarding this evaluation.
2. The Undersigned shall neither use the information
communicated by TransWeb nor circulate it within its own organization
except to the extent necessary to:
 - a. Participate in negotiations, discussions, and
consultations with personnel or authorized
representatives;
 - b. Supply TransWeb with goods or services at its
order;

CUSTOM MANUFACTURERS AND CONVERTERS OF ELECTRET AND MELT-BLOWN MEDIA

EXHIBIT A

BEST COPY

- c. Prepare estimates and proposals for submission to TransWeb.

3. The obligations of Paragraph 1 shall not apply to any of the information that the Undersigned can document:

- a. Was in the public domain at the time of communication by TransWeb;
- b. Entered the public domain subsequent to the time of communication by TransWeb through no fault of the Undersigned.
- c. Was in the Undersigned's possession free of any obligation of confidence at the time of communication by TransWeb.

4. All communicated materials, including without limitation, documents, drawings, models, apparatus, sketches, designs, and lists furnished by TransWeb, shall remain the property of TransWeb and shall be returned with all copies to TransWeb promptly at its request.

5. Communications from the Undersigned to personnel and authorized representatives of TransWeb shall be made on a confidential basis only.

6. The paragraphs of this Agreement are cumulative and severable.

7. In the event of a breach or threatened breach by the Undersigned of this Agreement, TransWeb will be entitled to an injunction restraining the Undersigned from such breach. Compliance with the Agreement is also a condition precedent to TransWeb's obligation to make any payments which might be otherwise payable to the Undersigned at the time of such breach. The Undersigned further agrees to indemnify and hold harmless TransWeb from all damages and

BEST COPY

costs, including reasonable attorney's fees, incurred by TransWeb arising out of the Undersigned's breach or threatened breach of this Agreement. Nothing in this Agreement shall be construed as prohibiting TransWeb from pursuing any other remedies for a breach or threatened breach of this Agreement.

8. The undersigned agrees not to publish evaluative data on confidential samples and agrees to circulate the data only to essential employees within their own companies.

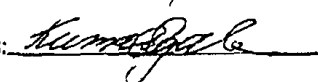
9. This Agreement shall be construed in accordance with the laws of the State of Maryland.

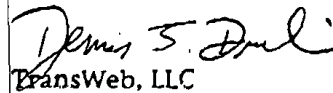

RACAL FILTERS

By: Pierre Legare

Title: Director Engineering

Date: June 2, 1997

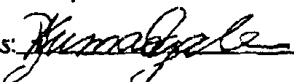
Witness: 


TransWeb, LLC

By: DENNIS S. DRAK

Title: VP SALES AND MARKETING

Date: 6/2/97

Witness: 

The following additional clauses are incorporated and form part of this agreement:

10. This agreement will cover confidential information pertaining to oily resistant thermoplastic media technology.

11. This agreement is subject to a term of 3 years from date of signing.

**CORPORATE RESEARCH LABORATORIES
CORPORATE ANALYTICAL TECHNOLOGY CENTER
SURFACE ANALYSIS**

Subject: Transweb T-Melt 30P Non-Woven Web

AR: AR 145596

To: J. S. Huberty
260-3B-08

Date: 2 December, 1998
Tel: 737-8310

X-ray photoelectron spectroscopy (ESCA) was performed on your samples. XPS is a surface sensitive non-damaging method of determining the elemental composition of the surface of materials ($Z > 1$) and is based on measuring the kinetic energy of photoemitted electrons from atomic core levels through soft x-ray excitation. Through energy conservation, the kinetic energy spectral density of photoemitted electrons is converted to an atomic binding energy distribution of emitted electrons and can thus be used to determine the elemental composition of the sampled material. XPS is quantitative and represents a sampling depth of between 5 and 50 Å depending upon the material being investigated and the electron kinetic energy of the emitted atomic core-level electron within the material. Detailed analysis of changes in core-level binding energy represent charge transfer in bonding environments and consequently, XPS can be used to determine surface chemistry.

Dr. J. S. Huberty, Occupational Health & Environmental Safety Division, submitted a sample of the non-woven web labeled Transweb T-Melt 30P. He requested that the chemical composition of the surface of the sample be determined, especially to determine the amount of fluorine present.

Measurements were performed on an HP-A ESCA system and on an SSI ESCA 200 System. The HP-A ESCA system excites photoelectrons using a monochromated Al x-ray source, emitted photoelectrons are detected at a 38° take-off angle with respect to the sample surface. The ESCA 200 system excites photoelectrons using a non-monochromated Al x-ray source, emitted photoelectrons are detected at a 65° take-off angle with respect to the sample surface. Spectra were obtained and the surface composition was determined by integrating the major peak areas and applying the appropriate sensitivity factors. The elemental compositions of these surfaces are as follows:

QC-ESCA Results

<u>Sample</u>	<u>Surface</u>	<u>Angle</u>	<u>C</u>	<u>Atom Percent</u>		<u>N</u>
				<u>O</u>	<u>F</u>	
T-melt 30P	web fibers	65	46	2.8	51	1.0

HP-A ESCA RESULTS

<u>Sample</u>	<u>Surface</u>	<u>Angle</u>	<u>C</u>	<u>Atom Percent</u>		<u>N</u>
				<u>O</u>	<u>F</u>	
T-melt 30P	web fibers	38	49	3.1	47	0.9

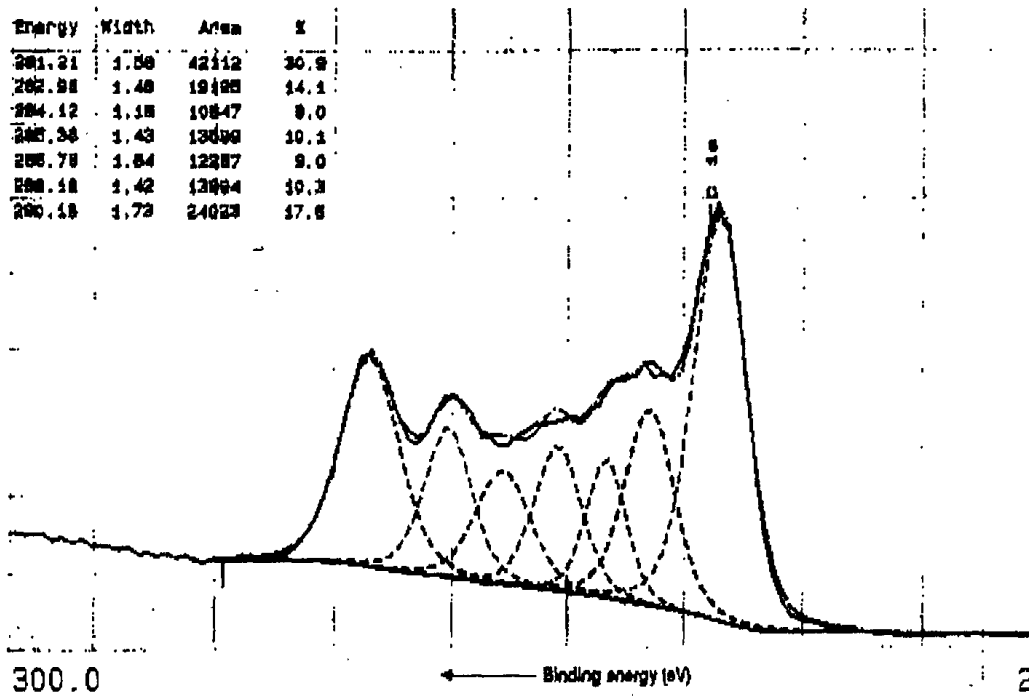
EXHIBIT B

BEST COPY

AR: 145596

Date: 2 December, 1998

Page 2

Carbon 1S Region - Transweb T-Melt 30P Fabric

The high resolution spectra of the carbon (1s) region indicates that the carbon spectra is comprised of several overlapping peaks indicative of the multiple states formed by exposure to a high energy plasma or corona type treatment. The presence of oxygen and nitrogen could suggest that the treatment had been carried out in air or in an inert atmosphere containing nitrogen.

Michael J. Prokosch
Senior Analytical Chemist
201-2S-16

733-2868

BEST COPY

Karl G. Hanson
Intellectual Property Counsel

Office of Intellectual
Property Counsel



April 28, 1999

Kumar Ogale
Transweb
1473 West Forest Grove Road
Vineland, NJ 08360

Dear Mr. Ogale:

Thank you for sending 3M the polymer samples that accompanied your March 26, 1999 letter to Gary Kurtzahn. 3M is holding these samples without any evaluation on its part, pending resolution of a matter outlined below in this letter.

In early 1998, 3M completed the purchase of the assets of a number of Racal companies including Racal Filter Technologies, Inc. The purchase of these businesses involved the assignment of various contracts to 3M, including a confidential nondisclosure agreement dated June 2, 1997 between Transweb, LLC and Racal Filter Technologies, Inc. As part of that agreement, samples were sent to Racal Filter Technologies for their evaluation. We are returning those samples to you with this letter because 3M presently does not have an interest in them in view of the new samples that you have recently provided us. 3M also would like to terminate the June 2, 1997 agreement with Transweb. 3M will, however, comply with the obligations imposed upon it by virtue of the agreement for information previously furnished to Racal. 3M does not consider the samples submitted with your March 26 letter to be submitted under the June 2 agreement but only under the more recent agreement dated February 24, 1999 between 3M and Transweb and Mr. Kurtzahn's March 15, 1999 letter to you.

If you agree to the foregoing, please acknowledge the same by signing one copy of this letter and returning it to 3M at your earliest convenience. You may retain one copy for your files.

Sincerely,

A handwritten signature in dark ink, appearing to read "Karl G. Hanson", written over a horizontal line.

Karl G. Hanson

KGH/smd

Minnesota Mining and
Manufacturing Company
PO Box 33427
St. Paul, MN 55133-3427 USA
651 736 7776
651 736 3833 Facsimile
kghanson@mmm.com E-mail

EXHIBIT C

EXHIBIT B



US006397458B1

(12) **United States Patent**
Jones et al.

(10) **Patent No.:** **US 6,397,458 B1**
(45) **Date of Patent:** **Jun. 4, 2002**

(54) **METHOD OF MAKING AN ELECTRET ARTICLE BY TRANSFERRING FLUORINE TO THE ARTICLE FROM A GASEOUS PHASE**

(75) Inventors: **Marvin E. Jones**, Grant Township; **Christopher S. Lyons**; **David B. Redmond**, both of St. Paul; **Jeffrey L. Solomon**, Vadnais Heights; **Seyed Abolhassan Angadjivand**, Woodbury, all of MN (US)

(73) Assignee: **3M Innovative Properties Company**, St. Paul, MN (US)

(*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 0 days.

(21) Appl. No.: **09/478,658**

(22) Filed: **Jan. 6, 2000**

Related U.S. Application Data

(62) Division of application No. 09/109,497, filed on Jul. 2, 1998.

(51) **Int. Cl.**⁷ **H01R 43/00**

(52) **U.S. Cl.** **29/825**; 29/592.1; 29/826

(58) **Field of Search** 29/825, 826, 592.1, 29/830, 832, 833

(56) References Cited

U.S. PATENT DOCUMENTS

3,994,258 A	11/1976	Simm
4,043,331 A	8/1977	Martin et al.
4,188,426 A	2/1980	Auerbach
4,215,682 A	8/1980	Kubik et al.
4,288,584 A	9/1981	Mishra
RE30,782 E	10/1981	van Turnhout
4,407,852 A	10/1983	Sapieha et al.
4,527,218 A	7/1985	von Seggern
4,588,537 A	5/1986	Klaase et al.
RE32,171 E	6/1986	van Turnhout
4,592,815 A	6/1986	Nakao
4,652,282 A	3/1987	Ohmori et al.
4,789,504 A	12/1988	Ohmori et al.
4,798,850 A	1/1989	Brown
4,874,399 A	10/1989	Reed et al.
4,874,659 A	10/1989	Ando et al.
5,025,052 A	6/1991	Crater et al.
5,057,710 A	10/1991	Nishiura et al.
5,099,026 A	3/1992	Crater et al.
5,110,620 A	5/1992	Tani et al.
5,304,227 A	4/1994	Matsuura et al.
5,370,830 A	12/1994	Jameson et al.

5,411,576 A	5/1995	Jones et al.
5,472,481 A	12/1995	Jones et al.
5,496,507 A	3/1996	Angadjivand et al.
5,554,722 A	9/1996	Eichenauer et al.
5,558,809 A	9/1996	Groh et al.
5,643,525 A	7/1997	McGinty et al.
5,645,627 A	7/1997	Lifshutz et al.
5,759,205 A	6/1998	Valentini
5,908,598 A	6/1999	Rousseau et al.
5,919,847 A	7/1999	Rousseau et al.
5,935,303 A	8/1999	Kimura
5,968,635 A	10/1999	Rousseau et al.
5,976,208 A	11/1999	Rousseau et al.
6,002,017 A	12/1999	Rousseau et al.

FOREIGN PATENT DOCUMENTS

EP	0 616 831 A1	8/1994
EP	0 615 007 A1	9/1994
EP	0 850 692 A1	7/1998
GB	2 060 259 A	4/1981
JP	60-947	4/1980
JP	60-15137	4/1985
JP	1-232038	9/1988
JP	8-57225	3/1996
WO	WO 96/26783	9/1996
WO	WO 97/07272	2/1997
WO	WO 98/58117	12/1998

OTHER PUBLICATIONS

Strobel, Mark, et al., *Plasma Fluorination of Polyolefins*, Journal of Polymer Science: Part A: Polymer Chemistry, vol. 25, 1295-1307 (1987).

Chudleigh, P.W., *Mechanism of Charge Transfer to a Polymer Surface By a Conducting Liquid Contact*, Journal of Applied Physics, vol. 47, No. 10, Oct. 1976.

Chudleigh, P. W., *Charging of Polymer Foils Using Liquid Contacts*, Appl. Phys. Lett. vol. 21, No. 11, Dec. 1, 1972.

Wente, *Superfine Thermoplastic Fibers*, Industrial and Engineering Chemistry, 48(8): 1342-1246 (1956).

Yatsuzuka, Kyoko, et al., *Electrification of Polymer Surface Caused by Sliding Ultrapure Water*, IEEE Transactions on Industry Applications, vol. 32, No. 4, Jul./Aug. 1996.

Derwent Publication of JP 08 057225 abstract (Mar. 5, 1996).

Derwent Publication of JP 05 253416 abstract (Oct. 5, 1993).

Primary Examiner—Carl J. Arbes

(74) *Attorney, Agent, or Firm*—Karl G. Hanson; Allison Johnson

(57) ABSTRACT

An electret is described that includes a surface modified polymeric article having surface fluorination produced by fluorinating the polymeric article.

58 Claims, 3 Drawing Sheets

U.S. Patent

Jun. 4, 2002

Sheet 1 of 3

US 6,397,458 B1

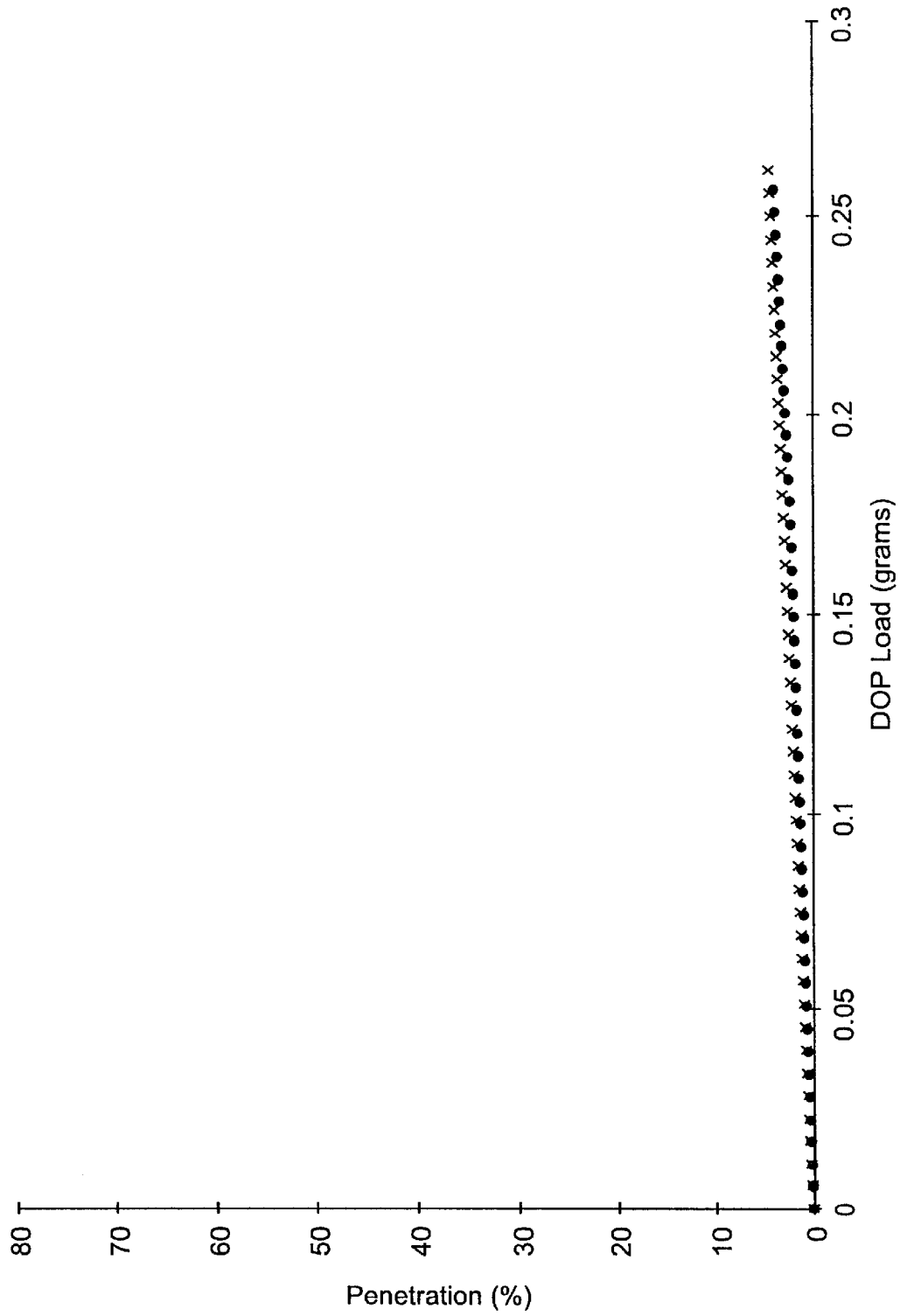


Fig. 1

U.S. Patent

Jun. 4, 2002

Sheet 2 of 3

US 6,397,458 B1

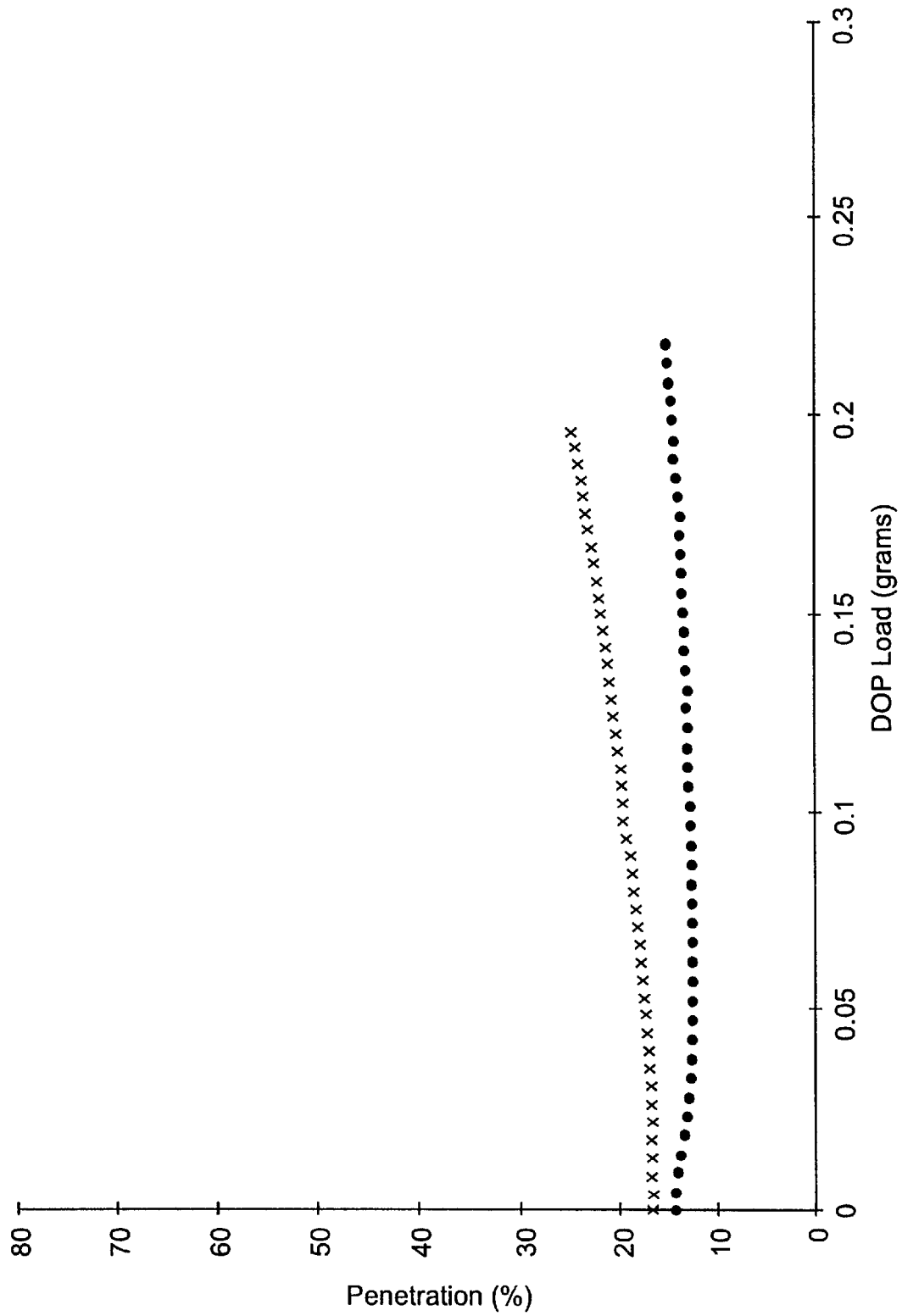


Fig. 2

U.S. Patent

Jun. 4, 2002

Sheet 3 of 3

US 6,397,458 B1

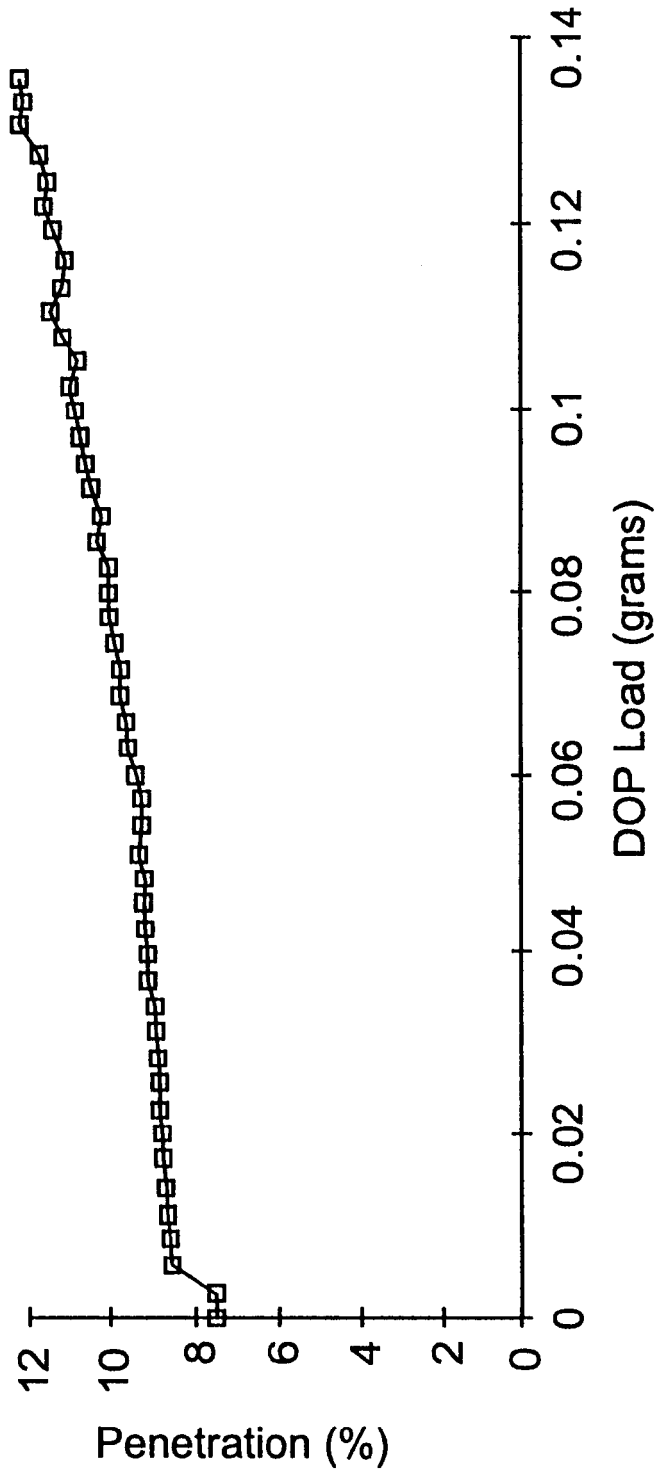


Fig. 3

US 6,397,458 B1

1

METHOD OF MAKING AN ELECTRET ARTICLE BY TRANSFERRING FLUORINE TO THE ARTICLE FROM A GASEOUS PHASE

This is a divisional of application Ser. No. 09/109,497 filed Jul. 2, 1998.

This invention relates to preparing fluorinated electrets.

BACKGROUND

The filtration properties of nonwoven polymeric fibrous webs can be improved by transforming the web into an electret, i.e., a dielectric material exhibiting a quasi-permanent electrical charge. Electrets are effective in enhancing particle capture in aerosol filters. Electrets are useful in a variety of devices including, e.g., air filters, face masks, and respirators, and as electrostatic elements in electro-acoustic devices such as microphones, headphones, and electrostatic recorders.

Electrets are currently produced by a variety of methods including direct current ("DC") corona charging (see, e.g., U.S. Pat. No. 30,782 (van Turnhout)), and hydrocharging (see, e.g., U.S. Pat. No. 5,496,507 (Angadjivand et al.)), and can be improved by incorporating fluorochemicals into the melt used to produce the fibers of some electrets (see, e.g., U.S. Pat. No. 5,025,052 (Crater et al.)).

Many of the particles and contaminants with which electret filters come into contact interfere with the filtering capabilities of the webs. Liquid aerosols, for example, particularly oily aerosols, tend to cause electret filters to lose their electret enhanced filtering efficiency (see, e.g., U.S. Pat. No. 5,411,576 (Jones et al.)).

Numerous methods have been developed to compensate for loss of filtering efficiency. One method includes increasing the amount of the nonwoven polymeric web in the electret filter by adding layers of web or increasing the thickness of the electret filter. The additional web, however, increases the breathing resistance of the electret filter, adds weight and bulk to the electret filter, and increases the cost of the electret filter. Another method for improving an electret filter's resistance to oily aerosols includes forming the electret filter from resins that include melt processable fluorochemical additives such as fluorochemical oxazolidinones, fluorochemical piperazines, and perfluorinated alkanes. (See, e.g., U.S. Pat. No. 5,025,052 (Crater et al.)). The fluorochemicals should be melt processable, i.e., suffer substantially no degradation under the melt processing conditions used to form the microfibers that are used in the fibrous webs of some electrets. (See, e.g., WO 97/07272 (Minnesota Mining and Manufacturing)).

SUMMARY OF THE INVENTION

In one aspect, the invention features an electret that includes a surface modified polymeric article having surface fluorination produced by fluorinating a polymeric article. In one embodiment, the article includes at least about 45 atomic % fluorine as detected by ESCA. In another embodiment, the article includes a $\text{CF}_3:\text{CF}_2$ ratio of at least about 0.25 as determined according to the Method for Determining $\text{CF}_3:\text{CF}_2$. In other embodiments, the article includes a $\text{CF}_3:\text{CF}_2$ ratio of at least about 0.45 as determined according to the Method for Determining $\text{CF}_3:\text{CF}_2$.

In one embodiment, the article has a Quality Factor of at least about 0.25/ mmH_2O , (preferably at least about 0.5/ mmH_2O , more preferably at least about 1/ mmH_2O).

In some embodiments, the article includes a nonwoven polymeric fibrous web. Examples of suitable fibers for the

2

nonwoven polymeric fibrous web include polycarbonate, polyolefin, polyester, halogenated polyvinyl, polystyrene, and combinations thereof. Particularly useful fibers include polypropylene, poly-(4-methyl-1-pentene), and combinations thereof. In one embodiment, the article includes melt-blown microfibers.

In another aspect, the invention features an electret that includes a polymeric article having at least about 45 atomic % fluorine as detected by ESCA, and a $\text{CF}_3:\text{CF}_2$ ratio of at least about 0.45 as determined according to the Method for Determining $\text{CF}_3:\text{CF}_2$. In another embodiment, the electret includes at least about 50 atomic % fluorine as detected by ESCA, and a $\text{CF}_3:\text{CF}_2$ ratio of at least about 0.25 as determined according to the Method for Determining $\text{CF}_3:\text{CF}_2$.

In other aspects, the invention features a respirator that includes the above-described electrets. In still other aspects, the invention features a filter that includes the above-described electrets.

In one aspect, the invention features a method of making an electret that includes: (a) fluorinating a polymeric article to produce an article having surface fluorination; and (b) charging the fluorinated article in a manner sufficient to produce an electret. In one embodiment, the method includes charging the fluorinated article by contacting the fluorinated article with water in a manner sufficient to produce an electret, and drying the article. The method is useful for making the above-described electrets. In another embodiment, the method includes charging the fluorinated article by impinging jets of water or a stream of water droplets onto the fluorinated article at a pressure and for a period sufficient to produce an electret, and drying the article.

In other embodiments, the method includes fluorinating a polymeric article in the presence of an electrical discharge (e.g., an alternating current corona discharge at atmospheric pressure) to produce a fluorinated article. In one embodiment, the method includes fluorinating the polymeric article in an atmosphere that includes fluorine containing species selected from the group consisting of elemental fluorine, fluorocarbons, hydrofluorocarbons, fluorinated sulfur, fluorinated nitrogen and combinations thereof. Examples of suitable fluorine containing species include C_5F_{12} , C_2F_6 , CF_4 , hexafluoropropylene, SF_6 , NF_3 , and combinations thereof.

In other embodiments, the method includes fluorinating the polymeric article in an atmosphere that includes elemental fluorine.

In other embodiments, the method of making the electret includes: (A) fluorinating a nonwoven polymeric fibrous web (i) in an atmosphere that includes fluorine containing species and an inert gas, and (ii) in the presence of an electrical discharge to produce a web having surface fluorination; and (B) charging the fluorinated web in a manner sufficient to produce an electret.

In other aspects, the invention features a method of filtering that includes passing an aerosol through the above-described electrets to remove contaminants.

The fluorinated electrets of the invention exhibit a relatively high oily mist resistance relative to non-fluorinated electrets.

GLOSSARY

In reference to the invention, these terms having the meanings set forth below:

US 6,397,458 B1

3

“electret” means a dielectric material exhibiting a quasi-permanent electrical charge. The term “quasi-permanent” means that the time constants characteristic for the decay of the charge are much longer than the time period over which the electret is used;

“surface modified” means that the chemical structure at the surface has been altered from its original state.

“surface fluorination” means the presence of fluorine atoms on a surface (e.g., the surface of an article);

“fluorine containing species” means molecules and moieties containing fluorine atoms including, e.g., fluorine atoms, elemental fluorine, and fluorine containing radicals;

“fluorinating” means placing fluorine atoms on the surface of an article by transferring fluorine containing species from a gaseous phase to the article by chemical reaction, sorption, condensation, or other suitable means;

“aerosol” means a gas that contains suspended particles in solid or liquid form; and

“contaminants” means particles and/or other substances that generally may not be considered to be particles (e.g., organic vapors).

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a plot of % DOP Penetration vs. DOP Load for Examples 36 and 37.

FIG. 2 is a plot of % DOP Penetration vs. DOP Load for Examples 38 and 39.

FIG. 3 is a plot of % DOP Penetration vs. DOP Load for Example 40.

DESCRIPTION OF PREFERRED EMBODIMENTS

The electret includes a surface modified polymeric article (e.g., a nonwoven polymeric fibrous web) produced by fluorinating a polymeric article. The electrets preferably have sufficient surface fluorination to provide oily mist resistance. One measure of oily mist resistance is how well the electret maintains its Quality Factor during challenge with an aerosol. The Quality Factor can be calculated from results obtained from the dioctylphthalate (“DOP”) initial penetration test (“the DOP test”). The DOP test also provides a relative measure of the charge state of the filter. The DOP test procedure involves forcing DOP aerosol at a face velocity of 6.9 cm/second for a period of about 30 seconds through the sample, measuring the pressure drop across the sample (Pressure Drop measured in mmH₂O) with a differential manometer, and measuring the percent DOP penetration (DOPPen %). The Quality Factor (QF) (measured in 1/mmH₂O) can be calculated from these values according to the following formula:

$$QF[1/\text{mmH}_2\text{O}] = \frac{-\ln \frac{\text{DOPPenetration}(\%)}{100}}{\text{PressureDrop}[\text{mmH}_2\text{O}]}$$

The higher the Quality Factor at a given flow rate, the better the filtering performance of the electret.

Preferred electrets have a Quality Factor of at least about 0.25/mmH₂O, preferably at least about 0.5/mmH₂O, more preferably at least about 1.0/mmH₂O.

Electron spectroscopy for chemical analysis (“ESCA”) (also known as X-ray photoelectron spectroscopy (“XPS”))

4

provides one measure of surface fluorination. Preferably the surface of the electret exhibits at least about 45 atomic % fluorine, more preferably at least about 50 atomic % fluorine when analyzed by ESCA. ESCA analyzes the elemental composition of the outermost surface (i.e., approximately 10 to 50 Å) of a specimen. ESCA can be used to detect all elements in the periodic table except helium and hydrogen.

The electret also has a CF₃:CF₂ ratio at the surface of the electret of at least about 0.25, preferably at least about 0.45, and more preferably greater than 0.9, as determined according to the Method For Determining CF₃:CF₂ ratio set forth in the Example section below.

In one embodiment, the electrets include nonwoven polymeric fibrous webs that include fibers such as, e.g., melt-blown microfibers, staple fibers, fibrillated films, and combinations thereof. The fibers can be formed from resins. Preferably the resin is a thermoplastic nonconductive, i.e., having a resistivity of greater than 10¹⁴ ohm-cm, resin. The resin used to form the fibers should be substantially free of materials such as antistatic agents that could increase the electrical conductivity or otherwise interfere with the ability of the fibers to accept and hold electrostatic charges.

Examples of useful thermoplastic resins include polyolefins such as, e.g., polypropylene, polyethylene, poly-(4-methyl-1-pentene), and combinations thereof, halogenated vinyl polymers (e.g., polyvinyl chloride), polystyrene, polycarbonates, polyesters, and combinations thereof.

Additives can be blended with the resin including, e.g., pigment, UV stabilizers, antioxidants, and combinations thereof.

Meltblown microfibers can be prepared as described in Wente, Van A., “Superfine Thermoplastic Fibers,” *Industrial Eng. Chemistry*, Vol. 48, pp. 1342–1346 and in Report No. 4364 of the Naval Research laboratories, published May 25, 1954, entitled, “Manufacture of Super Fine Organic Fibers,” by Wente et al. Meltblown microfibers preferably have an effective fiber diameter in the range of less than 1 to 50 μm as calculated according to the method set forth in Davies, C. N., “The Separation of Airborne Dust and Particles,” Institution of Mechanical Engineers, London, Proceedings 1B, 1952.

The presence of staple fibers provides a more lofty, less dense web than a web constructed solely of meltblown microfibers. Preferably the electret contains more than 70% by weight staple fibers. Webs containing staple fibers are disclosed in U.S. Pat. No. 4,118,531 (Hauser).

Electrets that include a nonwoven polymeric fibrous web preferably have a basis weight in the range of about 10 to 500 gm², more preferably about 10 to 100 gm². The thickness of the nonwoven polymeric fibrous web is preferably about 0.25 to 20 mm, more preferably about 0.5 to 2 mm.

The nonwoven polymeric webs of the electret can also include particulate matter as disclosed, for example, in U.S. Pat. No. 3,971,373, (Braun), U.S. Pat. No. 4,100,324 (Anderson), and U.S. Pat. No. 4,429,001 (Kolpin et al.).

Electret Preparation

The electrets can be prepared by fluorinating a polymeric article, optionally in the presence of a surface modifying electrical discharge, and charging the fluorinated article to produce an electret.

The fluorination process includes modifying the surface of the polymeric article to contain fluorine atoms by exposing the polymeric article to an atmosphere that includes fluorine containing species. The fluorination process can be performed at atmospheric pressure or under reduced pressure. The fluorination process is preferably performed in a controlled atmosphere to prevent contaminants from inter-

US 6,397,458 B1

5

fering with the addition of fluorine atoms to the surface of the article. The atmosphere should be substantially free of oxygen and other contaminants. Preferably the atmosphere contains less than 0.1% oxygen.

The fluorine containing species present in the atmosphere can be derived from fluorinated compounds that are gases at room temperature, become gases when heated, or are capable of being vaporized. Examples of useful sources of fluorine containing species include, fluorine atoms, elemental fluorine, fluorocarbons (e.g., C_5F_{12} , C_2F_6 , CF_4 , and hexafluoropropylene), hydrofluorocarbons (e.g., CF_3H), fluorinated sulfur (e.g., SF_6), fluorinated nitrogen (e.g., NF_3), fluorochemicals such as e.g., CF_3OCF_3 and fluorochemicals available under the trade designation Fluorinert such as, e.g., Fluorinert FC-43 (commercially available from Minnesota Mining and Manufacturing Company, Minnesota), and combinations thereof.

The atmosphere of fluorine containing species can also include an inert diluent gas such as, e.g., helium, argon, nitrogen, and combinations thereof.

The electrical discharge applied during the fluorination process is capable of modifying the surface chemistry of the polymeric article when applied in the presence of a source of fluorine containing species. The electrical discharge is in the form of plasma, e.g., glow discharge plasma, corona plasma, silent discharge plasma (also referred to as dielectric barrier discharge plasma and alternating current ("AC") corona discharge), and hybrid plasma, e.g., glow discharge plasma at atmospheric pressure, and pseudo glow discharge. Preferably the plasma is an AC corona discharge plasma at atmospheric pressure. Examples of useful surface modifying electrical discharge processes are described in U.S. Pat. Nos. 5,244,780, 4,828,871, and 4,844,979.

Another fluorination process includes immersing a polymeric article into a liquid that is inert with respect to elemental fluorine, and bubbling elemental fluorine gas through the liquid to produce a surface fluorinated article. Examples of useful liquids that are inert with respect to fluorine include perhalogenated liquids, e.g., perfluorinated liquids such as Performance Fluid PF 5052 (commercially available from Minnesota Mining and Manufacturing Company). The elemental fluorine containing gas that is bubbled through the liquid can include an inert gas such as, e.g., nitrogen, argon, helium, and combinations thereof.

Charging the polymeric article to produce an electret can be accomplished using a variety of techniques, including, e.g., hydrocharging, i.e., contacting an article with water in a manner sufficient to impart a charge to the article, followed by drying the article, and DC corona charging. The charging process can be applied to one or more surfaces of the article.

One example of a useful hydrocharging process includes impinging jets of water or a stream of water droplets onto the article at a pressure and for a period sufficient to impart a filtration enhancing electret charge to the web, and then drying the article. The pressure necessary to optimize the filtration enhancing electret charge imparted to the article will vary depending on the type of sprayer used, the type of polymer from which the article is formed, the type and concentration of additives to the polymer, and the thickness and density of the article. Pressures in the range of about 10 to about 500 psi (69 to 3450 kPa) are suitable. An example of a suitable method of hydrocharging is described in U.S. Pat. No. 5,496,507 (Angadjivand et al.).

The jets of water or stream of water droplets can be provided by any suitable spray device. One example of a useful spray device is the apparatus used for hydraulically entangling fibers.

6

Examples of suitable DC corona discharge processes are described in U.S. Pat. No. 30,782 (van Turnhout), U.S. Pat. No. 31,285 (van Turnhout), U.S. Pat. No. 32,171 (van Turnhout), U.S. Pat. No. 4,375,718 (Wadsworth et al.), U.S. Pat. No. 5,401,446 (Wadsworth et al.), U.S. Pat. No. 4,588,537 (Klasse et al.), and U.S. Pat. No. 4,592,815 (Nakao).

The fluorinated electrets formed by the methods described herein are suitable for use as, e.g., electrostatic elements in electro-acoustic devices such as microphones, headphones and speakers, fluid filters, dust particle control devices in, e.g., high voltage electrostatic generators, electrostatic recorders, respirators (e.g., prefilters, canisters and replaceable cartridges), heating, ventilation, air conditioning, and face masks.

The invention will now be described further by way of the following examples.

EXAMPLES

Test Procedures

Test procedures used in the examples include the following.

Method for Determining $CF_3:CF_2$

ESCA data was collected on a PHI 5100 ESCA system (Physical Electronics, Eden Prairie, Minn.) using a non-monochromatic $MgK\alpha$ x-ray source and a 45 degree electron takeoff angle with respect to the surface. The carbon (1s) spectra were peak fit using a nonlinear least-squares routine supplied by PHI (Physical Electronics, Eden Prairie, Minn.). This routine used a linear background subtraction, and a gaussian peak save for the component peaks. The spectra were referenced to the hydrocarbon peak at 285.0 eV. The CF_3 and CF_2 components were identified as the peaks located at about 294 eV and 292 eV respectively (according to the procedure described in Strobel et al., J. Polymer Sci. A: Polymer Chemistry, Vol. 25, pp. 1295-1307 (1987)). The $CF_3:CF_2$ ratio represent the ratio of the peak areas of the CF_3 and CF_2 components.

Initial Dioctylphthalate Penetration (DOP) and Pressure Drop Test Procedure

Initial DOP penetration is determined by forcing 0.3 micrometer diameter dioctyl phthalate (DOP) particles at a concentration of between 70 and 140 mg/m^3 (generated using a TSI No. 212 sprayer with four orifices and 30 psi clean air) through a sample of filter media which is 4.5 inches in diameter at a rate of 42.5 L/min (a face velocity of 6.9 centimeters per second). The sample is exposed to the DOP aerosol for 30 seconds until the readings stabilize. The penetration is measured with an optical scattering chamber, Percent Penetration Meter Model TPA-8F available from Air Techniques Inc.

Pressure drop across the sample is measured at a flow rate of 42.5 L/min (a face velocity of 6.9 cm/sec) using an electronic manometer. Pressure drop is reported in mm of water ("mm H_2O ").

DOP penetration and pressure drop are used to calculate the quality factor "QF" from the natural log (ln) of the DOP penetration by the following formula:

$$QF[1/mmH_2O] = \frac{-\ln \frac{DOP_{Penetration}(\%)}{100}}{PressureDrop[mmH_2O]}$$

A higher initial QF indicates better initial filtration performance. A decreased QF effectively correlates with decreased filtration performance.

DOP Loading Test

DOP loading is determined using the same test equipment used in the DOP penetration and pressure drop tests. The test

US 6,397,458 B1

7

sample is weighed and then exposed to the DOP aerosol for at least 45 min to provide a minimum exposure of at least about 130 mg. DOP penetration and pressure drop are measured throughout the test at least as frequently as once per minute. The mass of DOP collected is calculated for each measurement interval from the measured penetration, mass of the filter web, and total mass of DOP collected on the filter web during exposure ("DOP Load").
Corona Fluorination

Example 1

A blown polypropylene microfiber web prepared from Exxon 3505G polypropylene resin (Exxon Corp.) and having an effective fiber diameter of $7.5\ \mu\text{m}$ and a basis weight of $62\ \text{g/m}^2$ was prepared as described in Wentz, Van A., "Superfine Thermoplastic Fibers," *Industrial Eng. Chemistry*, Vol. 48, pp. 1342-1346.

The blown microfiber web was then AC corona fluorinated in a 1% by volume C_2F_6 in helium atmosphere at a corona energy of $34\ \text{J/cm}^2$, which corresponded to a corona power of 2000 W at a substrate speed of 1 m/min. The AC corona fluorination treatment was performed in an AC corona system that included the so-called "double-dielectric" electrode configuration with a ground roll consisting of 40 cm diameter nickel-plated aluminum roll covered with 1.5 mm of poly(ethylene terephthalate) and maintained at a temperature of 23°C . using recirculating, pressurized water. The powered electrodes consisted of 15 individual ceramic-covered electrodes (available from Sherman treaters Ltd., Thame, United Kingdom) each with a 15 mm square cross-section and an active length of 35 cm. The electrodes were connected to a model RS48-B (4 kW) variable-frequency power supply (available from ENI Power Systems Inc., Rochester, N.Y.). The net power dissipated in the AC corona was measured with a directional power meter incorporated into the ENI supply. The frequency of the output power was manually adjusted to about 16 kHz to obtain optimal impedance matching (minimum reflected power).

The AC corona system was enclosed within a controlled environment. Prior to treatment, the atmosphere surrounding the AC corona treatment system was purged with helium, and then continually flushed with 100 liters/min of 1% by volume C_2F_6 in helium, which was introduced near the electrodes.

The microfiber web was taped onto a carrier film of 0.05 mm thick bi-axially-oriented polypropylene (BOPP), and then placed on the ground roll such that the carrier film was in contact with the ground roll, causing one side of the blown microfiber web to be exposed to the discharge. After treatment, the blown microfiber web was flipped over, retaped to the carrier film, and AC corona treated a second time under the same conditions as the first treatment to expose the other side of the blown microfiber web to the discharge.

Example 2

A G100 Filtrete fibrillated film web (available from Minnesota Mining and Manufacturing), having a basis weight of $100\ \text{g/m}^2$, was corona fluorinated following the method described in Example 1, with the exception that the ground roll was maintained at a temperature of 25°C .

Example 3

A polyethylene meltblown microfiber web, prepared from Aspun PE-6806 polyethylene resin (DOW Chemical

8

Company, Michigan) and having a basis weight of $107\ \text{g/m}^2$, was corona fluorinated following the method described in Example 2.

Example 4

A polyester staple fiber web (available from Rogers Corporation), having a basis weight of $200\ \text{g/m}^2$, was corona fluorinated following the method described in Example 2.

Example 5

A poly-4-methyl-1-pentene meltblown microfiber web prepared from TPX MX-007 poly-4-methyl-1-pentene resin (Mitsui), and having a basis weight of $50\ \text{g/m}^2$ and an effective fiber diameter of $8.1\ \mu\text{m}$, was corona fluorinated following the method described in Example 2.

Examples 6-9

Examples 6-9 were prepared following the procedure in Example 1 except that the source of fluorine containing species was as follows: 1% CF_4 (Example 6), and 0.1% hexafluoropropylene (Example 7), 0.1% C_5F_{12} (Example 8), and 1.0% C_5F_{12} (Example 9).

The surface chemistry of each of the sample webs of Examples 1-9 was determined by ESCA analysis using a PHI 5100 ESCA system. The $\text{CF}_3:\text{CF}_2$ ratio was determined for each of the samples of Examples 1-9 from the ESCA data according to the above-described method. The results are reported in atomic % in Table I.

TABLE I

Example	Carbon	Nitrogen	Oxygen	Fluorine	$\text{CF}_3:\text{CF}_2$
1	43		5.7	51	1.09
2	44		6.2	50	1.37
3	49	0.2	8.2	42	1.10
4	42	0.5	7.8	49	0.99
5	44	0.0	2.9	53	1.19
6	41		3.5	55	0.86
7	41		2.7	56	0.97
8	42		6.4	52	0.91
9	43		5.2	51	0.89

Hydrocharging

Example 10

A fluorinated polypropylene blown microfiber web prepared as described above in Example 1, was passed over a vacuum slot at a rate of 5 cm/sec (centimeters/second) while deionized water was sprayed onto the web at a hydrostatic pressure of about 90 psi from a pair of Spraying Systems Teejet 9501 sprayer nozzles mounted 10 cm apart and centered 7 cm above the vacuum slot. The sample was then inverted and passed through the deionized water spray a second time such that both sides of the web were sprayed with water. The deionized water spray was then removed and the web was again passed over the vacuum slot to remove excess water. The web was then hung to dry at ambient conditions.

Example 11

A fluorinated poly-4-methyl-1-pentene meltblown microfiber web prepared according to Example 5 was charged following the procedure of Example 10.

Examples 10A-11A

Examples 10A-11A were prepared following the procedures of Example 10 and 11 respectively, with the exception

US 6,397,458 B1

9

that, after corona fluorination and prior to hydrocharging, each of the fluorinated webs of Examples 10A–11A were subjected to an anneal at 140° C. (300° F.) for about 10 minutes.

Examples 13, 15, 16, 18 and 20

Examples 13, 15, 16, 18 and 20 were charged following the procedure of Example 10, with the exception that the fluorinated polymeric fibrous webs used in each of Examples 13, 15, 16, 18 and 20 were as follows: a fluorinated polyethylene microfibr web prepared according to Example 3 above (Example 13); a fluorinated polyester staple fiber web prepared according to Example 4 (Example 15); a fluorinated G100 Filtrete fibrillated film web prepared according to Example 2 (Example 16); a fluorinated polypropylene needle punched web (12 denier/fiber fibers of Exxon 3505 polypropylene resin), having a basis weight of about 200 gm², and having been corona fluorinated following the method described in Example 1 (Example 18); and a polypropylene melt blown fine fiber web, having a basis weight of 46 gm² and an effective fiber diameter of 3.7 μm, and having been corona fluorinated following the method described in Example 1 with the exception that 0.2% C₅F₁₂ was used instead of 1% C₂F₆ (Example 20).

DC Corona Charging

Example 12

The fluorinated polyethylene meltblown microfibr web of Example 3 was charged using a DC corona discharge as follows. The fluorinated web was placed in contact with an aluminum ground plane, and then passed under an electrically positive DC corona source, in air, at a rate of about 1.2 meters/min, while maintaining a current to ground plane of about 0.01 mA/cm of corona source length. The distance from corona source to ground was about 4 cm.

Examples 14, 17, 19

Examples 14, 17 and 19 were charged following the procedure of Example 12, with the exception that the fluorinated polymeric fibrous webs for each of Examples 14, 17 and 19 were as follows: a fluorinated polyester staple fiber web prepared following the procedure of Example 4 (Example 14); a fluorinated polypropylene needle punched web (12 denier/fiber fibers made from Exxon 3505 polypropylene resin), having a basis weight of about 200 gm², and having been corona fluorinated following the method described in Example 1 (Example 17); and a fluorinated polypropylene meltblown fine fiber web, having a basis weight of 46 g/m² and an effective fiber diameter of 3.7 μm, and having been corona fluorinated following the method described in Example 1 with the exception that 0.2% C₅F₁₂ was used instead of 1% C₂F₆ (Example 19).

Example 21–35

Examples 21–35 were prepared by fluorinating polypropylene blown microfibr web following the procedure of Example 1, with the exception that the source of fluorine for each of Examples 21–35 was as follows: 1% CF₄ (Examples 21–23), 1% C₂F₆ (Examples 24–26), 0.1% hexafluoropropylene (Examples 27–29), 0.1% C₅F₁₂ (Examples 30–32), and 1.0% C₅F₁₂ (Examples 33–35).

The fluorinated webs of Examples 23, 26, 29, 32, and 35 were then charged following the hydrocharging process described above in Example 10.

The fluorinated webs of Examples 22, 25, 28, 31 and 34 were then charged following the DC corona charging process described above in Example 12.

10

% DOP penetration (“%DOP PEN”), Pressure Drop (mmH₂O), and the Quality Factor (“QF”) for each of the electrets of Examples 10–35 were determined according to the above-described Initial DOP Penetration and Pressure Drop Test Procedure. The results are summarized in Table II.

TABLE II

EXAMPLE	% DOP PEN	PRESSURE DROP	QF
10	0.119	3.65	1.84
10A	0.140	3.21	2.05
11	2.45	1.46	2.54
11A	0.778	1.60	3.04
12	56.1	1.14	0.51
13	38.1	1.15	0.84
14	78.3	0.38	0.64
15	65.6	0.41	1.03
16	27.3	0.40	3.25
17	70.4	0.19	1.85
18	37.6	0.19	5.15
19	0.81	10.58	0.46
20	0.006	11.3	0.86
21	55.6	2.83	0.21
22	15.0	3.28	0.58
23	0.288	3.09	1.89
24	54.1	3.05	0.20
25	14.3	3.32	0.59
26	0.243	3.08	1.95
27	59.0	2.81	0.19
28	16.2	2.80	0.65
29	0.276	2.90	2.03
30	52.5	3.15	0.20
31	14.0	3.11	0.63
32	0.250	2.99	2.00
33	45.3	3.10	0.26
34	14.9	2.93	0.65
35	0.244	3.14	1.92

Examples 36–39

Four fluorinated, polypropylene microfibr webs were prepared according to Example 1 with the exception that the source of fluorine containing species was as follows: 0.1% hexafluoropropylene (“HFP”) (Examples 36 and 38) and 0.1% C₅F₁₂ (Example 37 and 39).

Examples 36 and 37 further included charging the fluorinated polypropylene webs following the hydrocharging charging procedure of Example 10.

Examples 38 and 39 further included charging the fluorinated polypropylene webs following the DC corona charging procedure of Example 12.

Examples 36–39 were subjected to the above-described DOP Loading Test. The % DOP Penetration versus DOP loading (the amount of DOP collected on the web in grams) for each of Examples 36–39 was measured according to the above-described DOP Loading Test Procedure. The resulting data are plotted as % DOP penetration versus DOP load (grams) in FIGS. 1 and 2 as follows: Examples 36 and 37 (indicated with x’s and solid circles respectively) (FIG. 1), and Examples 38 and 39 (indicated with x’s and solid circles respectively) (FIG. 2).

Example 40

A 7 in. sample of polypropylene microfibr web having a basis weight 61 g/m² was placed under a nitrogen atmosphere. A gaseous mixture of 5% by volume elemental fluorine diluted in nitrogen was passed through the polypropylene microfibr web at a rate of 1.0 l/min for 10 minutes. The fluorine concentration was then increased to 10% by volume diluted in nitrogen and passed through the web at a rate of 1.0 l/min for an additional 20 minutes.

US 6,397,458 B1

11

The sample was then analyzed by ESCA and determined to have 62 atomic % fluorine and a $\text{CF}_3:\text{CF}_2$ ratio of 0.59, as determined according to the above-described Method for Determining $\text{CF}_3:\text{CF}_2$.

The sample was then charged using a DC corona discharge as described above in Example 12, and subjected to the above-described DOP Loading Test. The resulting data are plotted as % DOP Penetration versus DOP Load (grams) in FIG. 3.

Example 41

A polypropylene blown microfiber web, having a basis weight of 20 g/m² and a web width of 15 cm, was vacuum glow-discharge treated in a C_5F_{12} environment. The glow-discharge treatment was performed in a vacuum chamber. The vacuum chamber contained a roll-to-roll glow discharge system consisting of an unwind roller, glow discharge electrodes, and a windup roller for the continuous treatment of the blown microfiber web. Two stainless steel electrodes were in the parallel plate configuration, each electrode was 20 cm wide and 33 cm long and they were separated by a gap of 2.5 cm. The top electrode was grounded and the bottom electrode was powered by a 13.56 MHz rf generator (Plasma-Therm). The web traveled between the two electrodes and in contact with the top, grounded electrode so that one side of the web was exposed to the discharge.

After loading the roll of blown microfiber web onto the unwind roller under C_5F_{12} vapor at a pressure of 0.1 Torr. The blown microfiber web was advanced through the electrodes at a speed of 17 cm/min to achieve an exposure time to the plasma of 2 minutes. The discharge power was 50 W. After the first side was treated, the chamber was vented and the web roll replaced onto the unwind roller to allow the other side of the web to be treated. The treatment of the second side of the web occurred under the same conditions as the first side. After the fluorination, Example 41 was DC-corona charged following the process described above in Example 12.

% DOP Penetration (“%DOP PEN”) for Example 41 was determined according to the above-described Initial DOP Penetration and Pressure Drop Test Procedure. The results are summarized in Table III.

TABLE III

Loading Time (min)	% DOP Penetration Example 14
0.5	28
10	28

Other embodiments are within the following claims. Although the electret has been described reference to non-woven polymeric fibrous webs, the electret can be a variety of polymeric articles including, e.g., those polymeric articles described in U.S. patent application Ser. No. 09/106,506 entitled, “Structured Surface Filter Media,” (Insley et al.), filed on Jun. 18, 1998.

All of the patents and patent applications cited above are incorporated by reference into this document in total.

What is claimed is:

1. A method of making an electret comprising:
fluorinating a polymeric nonwoven web to produce an article having surface fluorination; and
charging the fluorinated web in a manner sufficient to produce an electret,

12

the electret comprising at least about 45 atomic % fluorine as detected by ESCA.

2. The method of claim 1, comprising charging the fluorinated article by contacting the fluorinated article with water in a manner sufficient to produce an electret, and drying the article.

3. The method of claim 1, comprising charging the fluorinated article by impinging jets of water or a stream of water droplets onto the fluorinated article at a pressure and for a period sufficient to produce an electret, and drying the article.

4. The method of claim 1, comprising fluorinating the polymeric nonwoven web in the presence of an electrical discharge to produce a fluorinated article.

5. The method of claim 4, comprising fluorinating the polymeric nonwoven web in the presence of an alternating current corona discharge at atmospheric pressure.

6. The method of claim 4, comprising fluorinating the polymeric nonwoven web in an atmosphere comprising fluorine containing species selected from the group consisting of elemental fluorine, fluorocarbons, hydrofluorocarbons, fluorinated sulfur, fluorinated nitrogen or a combination thereof.

7. The method of claim 6, wherein the fluorine containing species are selected from the group consisting of C_5F_{12} , C_2F_6 , CF_4 , hexafluoropropylene, SF_6 , NF_3 , or a combination thereof.

8. The method of claim 1, comprising fluorinating the polymeric nonwoven web in an atmosphere comprising elemental fluorine.

9. The method of claim 1, wherein the electret comprises a $\text{CF}_3:\text{CF}_2$ ratio of at least about 0.25 as determined according to the Method for Determining $\text{CF}_3:\text{CF}_2$.

10. The method of claim 1, wherein the electret comprises a $\text{CF}_3:\text{CF}_2$ ratio of at least about 0.45 as determined according to the Method for Determining $\text{CF}_3:\text{CF}_2$.

11. The method of claim 1, wherein the electret has a Quality Factor of at least about 0.25/mmH₂O.

12. The method of claim 1, comprising charging the fluorinated article with a direct current corona discharge to produce an electret.

13. The method of claim 1, further comprising annealing the fluorinated article prior to charging the fluorinated article.

14. The method of claim 1, wherein the electret comprises at least about 50 atomic % fluorine as detected by ESCA.

15. The method of claim 1, wherein the charged non-woven web has surface fluorination that comprises CF_3 and CF_2 at a $\text{CF}_3:\text{CF}_2$ ratio of at least 0.45 as determined according to the method for determining $\text{CF}_3:\text{CF}_2$.

16. The method of claim 1, wherein the charged non-woven web has surface fluorination that comprises CF_3 and CF_2 at a $\text{CF}_3:\text{CF}_2$ ratio of greater than 0.9 as determined according to the method for determining $\text{CF}_3:\text{CF}_2$.

17. A method of making an electret comprising:

- a) fluorinating a nonwoven polymeric fibrous web
 - i) in an atmosphere comprising fluorine containing species and an inert gas, and
 - ii) in the presence of an electrical discharge to produce a web having surface fluorination; and
 - b) charging the fluorinated web in a manner sufficient to produce an electret,
- the electret comprising at least about 45 atomic % fluorine as detected by ESCA.

18. A method of making an electret article, which method comprises the steps of:

US 6,397,458 B1

13

(a) providing a nonwoven fibrous web, wherein the fibers comprise a polymeric nonconductive thermoplastic resin;

(b) placing fluorine atoms on the surface of the polymeric fibers by transferring a fluorine-containing species from a gaseous phase to the fibers; and

(c) charging the fluorinated nonwoven fibrous web, the charged nonwoven web comprising at least about 45 atomic % fluorine as detected by ESCA.

19. The method of claim 18, wherein the fibers are fluorinated in the presence of a surface modifying electrical discharge.

20. The method of claim 19, wherein the gaseous phase includes an inert gas, the fluorine-containing species being present in the inert gas.

21. The method of claim 20, wherein the fluorination step is performed at atmospheric pressure.

22. The method of claim 20, wherein the fluorination step is performed at reduced pressure.

23. The method of claim 18, wherein the fluorination step is performed in a controlled atmosphere that prevents contaminants from interfering with the addition of fluorine atoms to the surface of the polymeric fibers.

24. The method of claim 23, wherein the controlled atmosphere is substantially free of oxygen and other contaminants.

25. The method of claim 24, wherein the controlled atmosphere contains less than 0.1 percent oxygen.

26. The method of claim 18, wherein the fluorine-containing species includes one or more of the following: fluorine atoms, elemental fluorine, fluorocarbons, hydrofluorocarbons, fluorinated sulfur, fluorinated nitrogen, CF_3OCF_3 , and combinations thereof.

27. The method of claim 26, wherein the inert gas is helium, argon, nitrogen, or a combination thereof.

28. The method of claim 19, wherein the surface modifying electrical discharge comprises the use of plasma.

29. The method of claim 18, wherein the fluorination step includes bubbling elemental fluorine gas through a liquid.

30. The method of claim 18, wherein the charging step includes hydrocharging, DC corona discharge, or a combination thereof.

31. The method of claim 30, wherein the charging step includes hydrocharging.

32. The method of claim 31, wherein the charging step includes DC corona discharge.

33. The method of claim 18, wherein the fibers are microfibers.

34. The method of claim 33, wherein the fibers are melt-blown microfibers that have an effective fiber diameter of 1 to 50 micrometers.

35. The method of claim 34, wherein the melt melt-blown microfibers comprise polypropylene resin and have a resistivity of greater than 10^{14} ohm*cm.

36. The method of claim 35, wherein the nonwoven web has a basis weight of 10 to 100 g/m² and has a thickness of 0.25 to 20 mm.

37. The method of claim 18, wherein the charged nonwoven web has a surface fluorination that comprises CF_3 and CF_2 at a $\text{CF}_3:\text{CF}_2$ ratio of at least 0.45 as determined according to the method for determining $\text{CF}_3:\text{CF}_2$.

38. The method of claim 37, wherein the nonwoven web comprises polymeric microfibers.

39. The method of claim 38, wherein the charged nonwoven web exhibits a Quality Factor of at least about 1.0 per mm H₂O.

14

40. The method of claim 37, wherein the charged nonwoven web has a $\text{CF}_3:\text{CF}_2$ ratio of at least 0.9.

41. The method of claim 38, wherein the microfibers are melt-blown microfibers that have an effective fiber diameter of 1 to 50 μm .

42. The method of claim 41, wherein the microfibers are made from a resin that has a resistivity greater than 10^{14} ohm-cm.

43. The method of claim 42, wherein the microfibers comprise a thermoplastic polyolefin.

44. The method of claim 43, wherein the microfibers comprise polypropylene.

45. The method of claim 44, wherein the nonwoven web has a basis weight of 10 to 100 g/m².

46. The method of claim 45, wherein the nonwoven web has a thickness of 0.25 to 20 mm.

47. The method of claim 46, wherein the nonwoven web has been fluorinated by transferring a fluorine containing species from a gaseous phase to the nonwoven web.

48. A method of making an electret comprising:

fluorinating a polymeric article to produce an article having surface fluorination;

annealing the fluorinated article; and

charging the fluorinated article in a manner sufficient to produce an electret.

49. A method of making an electret comprising:

fluorinating a polymeric article in the presence of an alternating current corona discharge at atmospheric pressure to produce an article having surface fluorination; and

charging the fluorinated article in a manner sufficient to produce an electret.

50. A method of making an electret comprising:

fluorinating a polymeric article at atmospheric pressure to produce an article having surface fluorination; and

charging the fluorinated article in a manner sufficient to produce an electret.

51. A method of making an electret comprising:

fluorinating a polymeric article to produce an article having surface fluorination; and

charging the fluorinated article in a manner sufficient to produce an electret,

the electret having a quality factor of at least 1.0/mmH₂O.

52. The method of claim 51, wherein the electret has a Quality Factor of at least 1.5/mmH₂O.

53. The method of claim 51, wherein the electret has a Quality Factor of at least 2/mmH₂O.

54. The method of claim 51, wherein the electret has a Quality Factor of at least 3/mmH₂O.

55. The method of claim 51, wherein the electret has a Quality Factor of at least 5/mmH₂O.

56. A method of making an electret article, which method comprises the steps of:

(a) providing a nonwoven fibrous web, wherein the fibers comprise a polymeric nonconductive thermoplastic resin;

(b) placing fluorine atoms on the surface of the polymeric fibers by transferring a fluorine-containing species from a gaseous phase to the fibers; and

(c) charging the fluorinated nonwoven fibrous web, the charged nonwoven web having a surface fluorination that comprises CF_3 and CF_2 at a $\text{CF}_3:\text{CF}_2$ ratio of at least 0.45 as determined according to the method for determining $\text{CF}_3:\text{CF}_2$.

US 6,397,458 B1

15

57. A method of making an electret article, which method comprises the steps of:

- (a) providing a nonwoven fibrous web, wherein the fibers comprise a polymeric nonconductive thermoplastic resin;
- (b) placing fluorine atoms on the surface of the polymeric fibers by transferring a fluorine-containing species from a gaseous phase to the fibers; and
- (c) charging the fluorinated nonwoven fibrous web, the charged nonwoven web exhibiting a Quality Factor of at least about 1.0/mmH₂O.

16

58. A method of making an electret article, which method comprises the steps of:

- (a) providing a nonwoven fibrous web, wherein the fibers comprise a polymeric nonconductive thermoplastic resin;
- (b) bubbling elemental fluorine gas through a liquid;
- (c) placing fluorine atoms on the surface of the polymeric fibers by transferring a fluorine-containing species from a gaseous phase to the fibers; and
- (d) charging the fluorinated nonwoven fibrous web.

* * * * *

UNITED STATES PATENT AND TRADEMARK OFFICE
CERTIFICATE OF CORRECTION

PATENT NO. : 6,397,458 B1
DATED : June 4, 2002
INVENTOR(S) : Jones, Marvin E.

Page 1 of 1

It is certified that error appears in the above-identified patent and that said Letters Patent is hereby corrected as shown below:

Column 3,

Line 64, "0.5/mmH₂O" should read as -- 0.5/mmH₂O --.

Column 4,

Line 49, both occurrences of "gm²" should read as -- g/m² --.

Column 9,

Line 18, "about:200" should read as -- about 200 --.


Lines 21 and 45, "gm²" should read as -- g/m² --.

Column 10,

Line 60, after "in." insert -- by 7in. --.

Signed and Sealed this

Third Day of December, 2002

A handwritten signature in black ink, appearing to read "James E. Rogan", with a horizontal line drawn underneath it.

JAMES E. ROGAN
Director of the United States Patent and Trademark Office

UNITED STATES PATENT AND TRADEMARK OFFICE
CERTIFICATE OF CORRECTION

PATENT NO. : 6,397,458 B1
DATED : June 4, 2002
INVENTOR(S) : Jones et al.

Page 1 of 1

It is certified that error appears in the above-identified patent and that said Letters Patent is hereby corrected as shown below:

Column 6,

Line 29, "save" should read -- shape --.

Column 13,

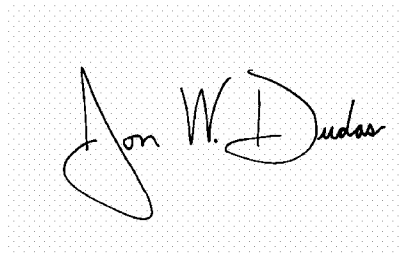
Line 23, between "of" and "fluorine" insert -- the --.

Line 46, "31" should read -- 18 --.

Line 55, "ohm*cm." should read -- ohm·cm. --.

Signed and Sealed this

Twentieth Day of December, 2005

A handwritten signature in black ink on a light gray dotted background. The signature reads "Jon W. Dudas" in a cursive, stylized script. The first name "Jon" is written with a large, sweeping initial 'J'. The last name "Dudas" is written with a large, sweeping initial 'D'.

JON W. DUDAS

Director of the United States Patent and Trademark Office

EXHIBIT C

PATENT
Docket No.: 53205USA7A.002

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of:

MARVIN E. JONES ET AL.

Serial No.: 09/109,497

Filed: July 2, 1998

For: FLUORINATED ELECTRET

Group Art Unit: 1724

Examiner: Richard L. Chiesa

SUPPLEMENTAL INFORMATION DISCLOSURE STATEMENT
PROPRIETARY MATERIAL

Assistant Commissioner for Patents
Washington, D.C. 20231

Dear Sir:

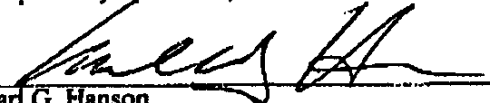
On June 2, 1997, Racal Filter Technologies, Inc. (Racal) entered into a Confidential Disclosure Agreement (Exhibit A) with Transweb, LLC. As part of this arrangement between the parties, Transweb furnished to Racal a sample of a nonwoven filtration web. The web was accompanied by a product sheet that outlined the filtration properties of a product designated as Tmelt 30P (Exhibit B).

In early 1998, 3M acquired the assets of Racal Filter. As part of the purchase of Racal's assets, 3M obtained possession of the Transweb product that was submitted under the Confidential Disclosure Agreement dated June 2, 1997. This product was subsequently analyzed by 3M's corporate research laboratories, and a report was prepared, dated December 2, 1998. The product that was received from Transweb contained polymeric fibers, which were believed to be microfibers. The surface fluorination on the product was analyzed, and the results of the analysis are set forth in the 3M internal report dated December 2, 1998. Based on the inventors' review of the data set forth in the report, it is believed that the Transweb product had a $\text{CF}_3:\text{CF}_2$ ratio of at least 0.45, and possibly greater than 0.9. The quality factor for this product is believed to be somewhere between 0.13 and 0.62, based on the data supplied in the Transweb product sheet. The basis weight for the product was determined to be 30 g/m².

Although 3M acquired Racal prior to the filing date of the present application, neither the Transweb Tmelt 30P product, nor the product sheet, was shown or otherwise known to the inventors named in this patent application, or the undersigned, before the July 2, 1998 filing date of this patent application. The product is no longer in 3M's possession. It was returned to Transweb along with a letter dated April 28, 1999 (Exhibit C). The applicants are unaware of any public disclosure of the Tmelt 30P product before the July 2, 1998 filing date. Applicants do believe, however, that the product may have been subsequently commercialized by Transweb. No patent applications are believed to have been filed by Transweb for this product.

Dated this 1st day of November, 2000.

Respectfully submitted,


Karl G. Hanson
Attorney for Applicants
Registration No. 32,900

3M Office of Intellectual Property Counsel
3M Innovative Properties Company
P.O. Box 33427
St. Paul, Minnesota 55133-3427
Telephone: (651) 736-7776
Facsimile: (651) 736-3833



CONFIDENTIAL
Non-Disclosure Agreement

TransWeb, LLC
1473 West Forest Grove Rd.
Vineland, New Jersey 08360
Telephone 609-205-1313
Facsimile 609-205-1333

This Agreement is made this 24 of June, 1997
between TransWeb, LLC, herein referred to as "TransWeb" and
PRIME FILTER TECHNOLOGIES, INC., herein
referred to as "The Undersigned".

This Agreement entails any and all matters seen, heard, or
learned during any visit to and/or communications with TransWeb.

The Undersigned acknowledges that in its course of dealings with
TransWeb, the Undersigned will receive specialized knowledge which, if
used in competition with TransWeb, could cause serious harm to
TransWeb.

In consideration of trade secret information provided by
TransWeb to the Undersigned and secret information provided to the
Undersigned by TransWeb, for various business purposes, the parties
agree:-

1. The Undersigned shall not communicate to any third party,
directly or indirectly, any confidential information received from
TransWeb, whether written or otherwise regarding this evaluation.

2. The Undersigned shall neither use the information
communicated by TransWeb nor circulate it within its own organization
except to the extent necessary to:

- a. Participate in negotiations, discussions, and
consultations with personnel or authorized
representatives;
- b. Supply TransWeb with goods or services at its
order;

CUSTOM MANUFACTURERS AND CONVERTERS OF ELECTRET AND MELTDOWN MEDIA

EXHIBIT A

- c. Prepare estimates and proposals for submission to TransWeb.

3. The obligations of Paragraph 1 shall not apply to any of the information that the Undersigned can document:

- a. Was in the public domain at the time of communication by TransWeb;
- b. Entered the public domain subsequent to the time of communication by TransWeb through no fault of the Undersigned.
- c. Was in the Undersigned's possession free of any obligation of confidence at the time of communication by TransWeb.

4. All communicated materials, including without limitation, documents, drawings, models, apparatus, sketches, designs, and lists furnished by TransWeb, shall remain the property of TransWeb and shall be returned with all copies to TransWeb promptly at its request.

5. Communications from the Undersigned to personnel and authorized representatives of TransWeb shall be made on a confidential basis only.

6. The paragraphs of this Agreement are cumulative and severable.

7. In the event of a breach or threatened breach by the Undersigned of this Agreement, TransWeb will be entitled to an injunction restraining the Undersigned from such breach. Compliance with the Agreement is also a condition precedent to TransWeb's obligation to make any payments which might be otherwise payable to the Undersigned at the time of such breach. The Undersigned further agrees to indemnify and hold harmless TransWeb from all damages and

costs, including reasonable attorney's fees, incurred by TransWeb arising out of the Undersigned's breach or threatened breach of this Agreement. Nothing in this Agreement shall be construed as prohibiting TransWeb from pursuing any other remedies for a breach or threatened breach of this Agreement.

8. The undersigned agrees not to publish evaluative data on confidential samples and agrees to circulate the data only to essential employees within their own companies.

9. This Agreement shall be construed in accordance with the laws of the State of Maryland.

Pierre Legare
RACAL FILTERS

By: Pierre Legare

Title: Director Engineering

Date: June 2, 1997

Witness: Humboldt

Dennis S. Drak
TransWeb, LLC

By: DENNIS S. DRAKE

Title: VP SALES AND MARKETING

Date: 6/2/97

Witness: Humboldt

The following additional clauses are incorporated and form part of this agreement:

10. This agreement will cover confidential information pertaining to oily resistant thermoplastic media technology.

11. This agreement is subject to a term of 3 years from date of signing.

CORPORATE RESEARCH LABORATORIES
CORPORATE ANALYTICAL TECHNOLOGY CENTER
SURFACE ANALYSIS

Subject: Transweb T-Melt 30P Non-Woven Web

AR: AR 146596

To: J. S. Huberty
260-38-08

Date: 2 December, 1998
Tel: 737-8310

X-ray photoelectron spectroscopy (ESCA) was performed on your samples. XPS is a surface sensitive non-damaging method of determining the elemental composition of the surface of materials ($Z > 1$) and is based on measuring the kinetic energy of photoemitted electrons from atomic core levels through soft x-ray excitation. Through energy conservation, the kinetic energy spectral density of photoemitted electrons is converted to an atomic binding energy distribution of emitted electrons and can thus be used to determine the elemental composition of the sampled material. XPS is quantitative and represents a sampling depth of between 5 and 50 Å depending upon the material being investigated and the electron kinetic energy of the emitted atomic core-level electron within the material. Detailed analysis of changes in core-level binding energy represent charge transfer in bonding environments and consequently, XPS can be used to determine surface chemistry.

Dr. J. S. Huberty, Occupational Health & Environmental Safety Division, submitted a sample of the non-woven web labeled Transweb T-Melt 30P. He requested that the chemical composition of the surface of the sample be determined, especially to determine the amount of fluorine present.

Measurements were performed on an HP-A ESCA system and on an SSI ESCA 200 System. The HP-A ESCA system excites photoelectrons using a monochromated Al x-ray source, emitted photoelectrons are detected at a 38° take-off angle with respect to the sample surface. The ESCA 200 system excites photoelectrons using a non-monochromated Al x-ray source, emitted photoelectrons are detected at a 65° take-off angle with respect to the sample surface. Spectra were obtained and the surface composition was determined by integrating the major peak areas and applying the appropriate sensitivity factors. The elemental compositions of these surfaces are as follows:

QC-ESCA Results

Sample	Surface	Angle	C	Atom Percent		
				O	F	N
T-melt 30P	web fibers	65	48	2.8	51	1.0

HP-A ESCA RESULTS

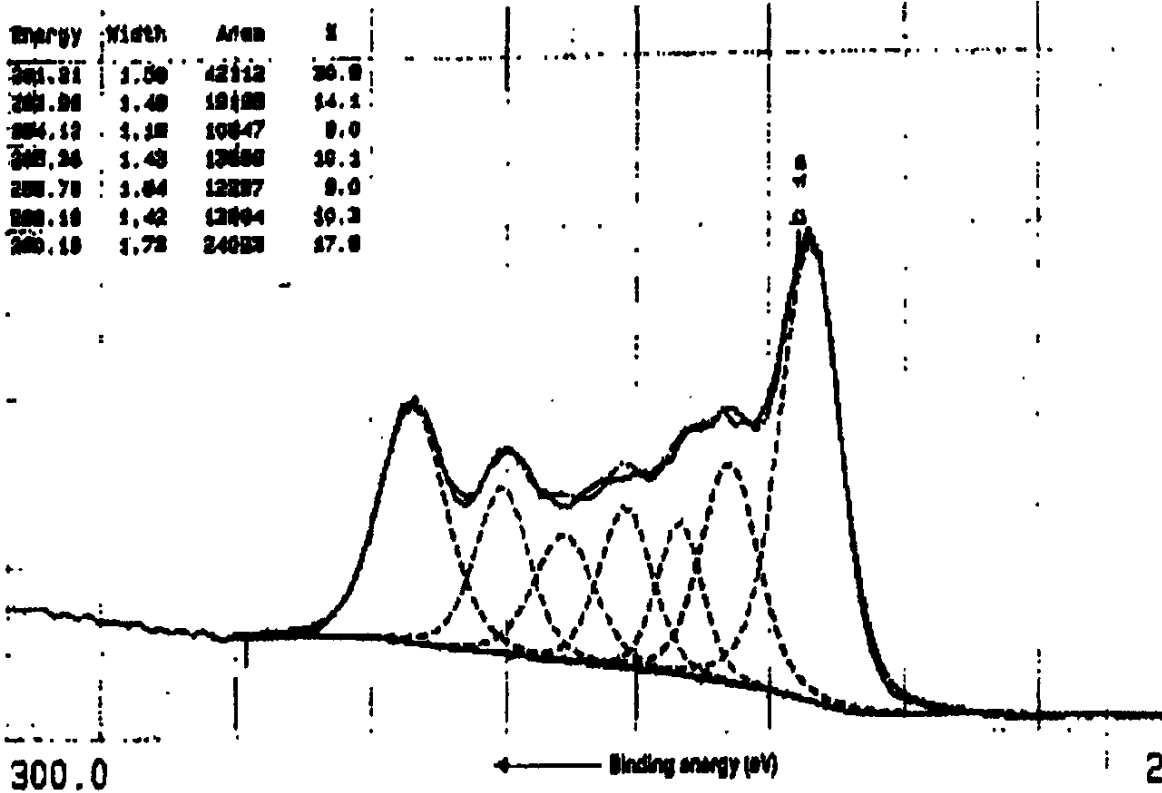
Sample	Surface	Angle	C	Atom Percent		
				O	F	N
T-melt 30P	web fibers	38	49	3.1	47	0.9

EXHIBIT B

AR: 146596

Date: 2 December, 1998

Page 2



Carbon 1S Region - Transweb T-Melt 30P Fabric

The high resolution spectra of the carbon (1s) region indicates that the carbon spectra is comprised of several overlapping peaks indicative of the multiple states formed by exposure to a high energy plasma or corona type treatment. The presense of oxygen and nitrogen could suggest that the treatment had been carried out in air or in an inert atmosphere containing nitrogen.

Michael J. Prokosch
Senior Analytical Chemist
201-29-16

733-2868

Karl G. Hanson
Intellectual Property Counsel

Office of Intellectual
Property Counsel



April 28, 1999

Kumar Ogale
Transweb
1473 West Forest Grove Road
Vineland, NJ 08360

Dear Mr. Ogale:

Thank you for sending 3M the polymer samples that accompanied your March 26, 1999 letter to Gary Kurtzahn. 3M is holding these samples without any evaluation on its part, pending resolution of a matter outlined below in this letter.

In early 1998, 3M completed the purchase of the assets of a number of Racal companies including Racal Filter Technologies, Inc. The purchase of these businesses involved the assignment of various contracts to 3M, including a confidential nondisclosure agreement dated June 2, 1997 between Transweb, LLC and Racal Filter Technologies, Inc. As part of that agreement, samples were sent to Racal Filter Technologies for their evaluation. We are returning those samples to you with this letter because 3M presently does not have an interest in them in view of the new samples that you have recently provided us. 3M also would like to terminate the June 2, 1997 agreement with Transweb. 3M will, however, comply with the obligations imposed upon it by virtue of the agreement for information previously furnished to Racal. 3M does not consider the samples submitted with your March 26 letter to be submitted under the June 2 agreement but only under the more recent agreement dated February 24, 1999 between 3M and Transweb and Mr. Kurtzahn's March 15, 1999 letter to you.

If you agree to the foregoing, please acknowledge the same by signing one copy of this letter and returning it to 3M at your earliest convenience. You may retain one copy for your files.

Sincerely,

A handwritten signature in black ink, appearing to read "Karl G. Hanson".

Karl G. Hanson

KGH/and

Minnesota Mining and
Manufacturing Company
PO Box 33427
St. Paul, MN 55133-3427 USA
651 736 7776
651 736 3833 Facsimile
kghanson@mmmc.com E-mail

EXHIBIT C

EXHIBIT D



US006808551B2

(12) **United States Patent**
Jones et al.

(10) **Patent No.:** **US 6,808,551 B2**
(45) **Date of Patent:** **Oct. 26, 2004**

(54) **METHOD OF USING FLUORINATED ELECTRETS**

(75) Inventors: **Marvin E. Jones**, Grant Township, MN (US); **Christopher S. Lyons**, St. Paul, MN (US); **David B. Redmond**, St. Paul, MN (US); **Jeffrey L. Solomon**, Vadnais Heights, MN (US); **Seyed Abolhassan Angadjivand**, Woodbury, MN (US)

(73) Assignee: **3M Innovative Properties Company**, St. Paul, MN (US)

(*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 0 days.

(21) Appl. No.: **10/681,670**

(22) Filed: **Oct. 7, 2003**

(65) **Prior Publication Data**

US 2004/0065196 A1 Apr. 8, 2004

Related U.S. Application Data

(63) Continuation of application No. 10/391,240, filed on Mar. 18, 2003, now Pat. No. 6,660,210, which is a continuation of application No. 10/126,028, filed on Apr. 19, 2002, now Pat. No. 6,562,112, which is a continuation of application No. 09/109,497, filed on Jul. 2, 1998, now Pat. No. 6,432,175.

(51) **Int. Cl.**⁷ **B03C 3/28**

(52) **U.S. Cl.** **95/59; 55/528; 55/DIG. 39; 96/69**

(58) **Field of Search** **95/57, 59; 96/15, 96/66-69; 55/528, DIG. 39**

(56) **References Cited**

U.S. PATENT DOCUMENTS

3,994,258 A 11/1976 Simm
4,043,331 A 8/1977 Martin et al.
4,118,531 A 10/1978 Hauser

4,215,682 A 8/1980 Kubik et al.
4,288,584 A 9/1981 Mishra
RE30,782 E 10/1981 Van Turnhout
4,375,718 A 3/1983 Wadsworth et al.
RE31,285 E 6/1983 Van Turnhout
4,407,852 A 10/1983 Sapieha et al.
4,527,218 A 7/1985 von Seggern
4,588,537 A * 5/1986 Klaase et al. 264/436
RE32,171 E 6/1986 Van Turnhout
4,592,815 A 6/1986 Nakao
4,652,282 A 3/1987 Ohmori et al.
4,789,504 A 12/1988 Ohmori et al.
4,798,850 A 1/1989 Brown
4,874,399 A * 10/1989 Reed et al. 95/57
4,874,659 A 10/1989 Ando et al.
5,025,052 A 6/1991 Crater et al.
5,057,710 A 10/1991 Nishiura et al. 307/400
5,099,026 A 3/1992 Crater et al.
5,110,620 A 5/1992 Tani et al.
5,244,780 A * 9/1993 Strobel et al. 430/535
5,304,227 A 4/1994 Matsura et al. 55/524
5,370,830 A 12/1994 Jameson et al. 264/23
5,411,576 A * 5/1995 Jones et al. 95/57

(List continued on next page.)

FOREIGN PATENT DOCUMENTS

EP 0 615 007 A1 9/1994
EP 0 616 831 A1 9/1994
EP 0 850 692 A1 7/1998

(List continued on next page.)

OTHER PUBLICATIONS

Strobel, Mark, et al, "Plasma Fluorination of Polyolefins," Journal of Polymer Science: Part A: Polymer Chemistry, vol. 25, 1295-1307 (1987).*

(List continued on next page.)

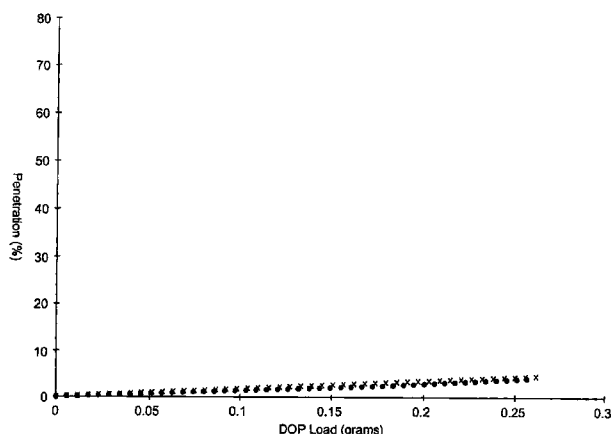
Primary Examiner—Richard L. Chiesa

(74) *Attorney, Agent, or Firm*—Karl Hanson; Allison Johnson

(57) **ABSTRACT**

An electret is described that includes a surface modified polymeric article having surface fluorination produced by fluorinating the polymeric article.

37 Claims, 3 Drawing Sheets



US 6,808,551 B2

Page 2

U.S. PATENT DOCUMENTS

5,437,900 A * 8/1995 Kuzowski 428/36.1
 5,472,481 A * 12/1995 Jones et al. 96/15
 5,496,507 A * 3/1996 Angadjivand et al. 264/423
 5,554,722 A 9/1996 Eichenauer et al. 528/340
 5,558,809 A 9/1996 Groh et al. 252/62.54
 5,643,525 A 7/1997 McGinty et al. 264/469
 5,645,627 A * 7/1997 Lifshutz et al. 96/15
 5,759,205 A 6/1998 Valentini 623/16
 5,830,810 A * 11/1998 Cohen 442/110
 5,908,598 A 6/1999 Rousseau et al. 264/344
 5,919,847 A 7/1999 Rousseau et al. 524/89
 5,935,303 A * 8/1999 Kimura 96/69
 5,964,926 A * 10/1999 Cohen 96/15
 5,968,635 A 10/1999 Rousseau et al. 428/198
 5,976,208 A * 11/1999 Rousseau et al. 55/385.3
 6,002,017 A 12/1999 Rousseau et al. 548/451
 6,068,799 A 5/2000 Rousseau et al. 264/6
 6,119,691 A 9/2000 Angadjivand et al. . 128/206.19
 6,123,752 A * 9/2000 Wu et al. 96/69
 6,213,122 B1 4/2001 Rousseau et al. 128/206.19
 6,214,094 B1 4/2001 Rousseau et al. 96/15
 6,237,595 B1 5/2001 Rousseau et al. 128/206.19
 6,238,466 B1 5/2001 Rousseau et al. 95/15
 6,261,342 B1 7/2001 Rousseau et al. 95/59
 6,268,495 B1 7/2001 Rousseau et al. 544/197
 6,319,452 B1 11/2001 Rousseau et al. 264/464
 6,375,886 B1 4/2002 Angadjivand et al. 264/460
 6,397,458 B1 6/2002 Jones et al. 29/825
 6,398,847 B1 6/2002 Jones et al. 95/57
 6,406,657 B1 6/2002 Eitzman et al. 264/340
 6,409,806 B1 6/2002 Jones et al. 96/15
 6,419,871 B1 * 7/2002 Ogale 264/423
 6,432,175 B1 * 8/2002 Jones et al. 96/15
 6,454,986 B1 9/2002 Eitzman et al. 264/442
 6,562,112 B2 * 5/2003 Jones et al. 96/15
 6,660,210 B2 * 12/2003 Jones et al. 264/423

FOREIGN PATENT DOCUMENTS

GB 2060259 A 4/1981
 JP 60-947 4/1980
 JP 60-15137 4/1985
 JP 1-232038 * 9/1989 96/69
 JP 05-253416 10/1993
 JP 8-57225 3/1996
 WO WO 96/26783 9/1996
 WO WO 97/07272 2/1997
 WO WO 98/58117 12/1998

OTHER PUBLICATIONS

Strobel, Mark, et al., "Plasma Fluorination of Polyolefins," Journal of Polymer Science: Part A: Polymer Chemistry, vol. 25, 1295–1307 (1987).

Chudleigh, P.W., "Mechanism of Charge Transfer to a Polymer Surface by a Conducting Liquid Contact," Journal of Applied Physics, vol. 47, No. 10, Oct. 1976.

Chudleigh, P.W., "Charging of Polymer Foils Using Liquid Contacts," Appl. Phys. Lett., vol. 21, No. 11, Dec. 1, 1972.

Yatsuzuka, Kyoko, et al., "Electrification of Polymer Surface Caused by Sliding Ultrapure Water," IEEE Transactions on Industry Applications, vol. 32, No. 4, Jul./Aug. 1996.

Wente, "Superfine Thermoplastic Fibers," Industrial and Engineering Chemistry, 48(8):1342–46 (1956).

U.S. patent application Ser. No. 09/111,833, filed Sep. 2, 1997.

Supplemental Information Disclosure Statement (2 pages); Exhibit A, Transweb LLC–Racal Filter Technologies, Inc. Agreement (3 pages), Exhibit B (2 pages), Exhibit C (1 page), Jun. 2, 1997.

* cited by examiner

U.S. Patent

Oct. 26, 2004

Sheet 1 of 3

US 6,808,551 B2

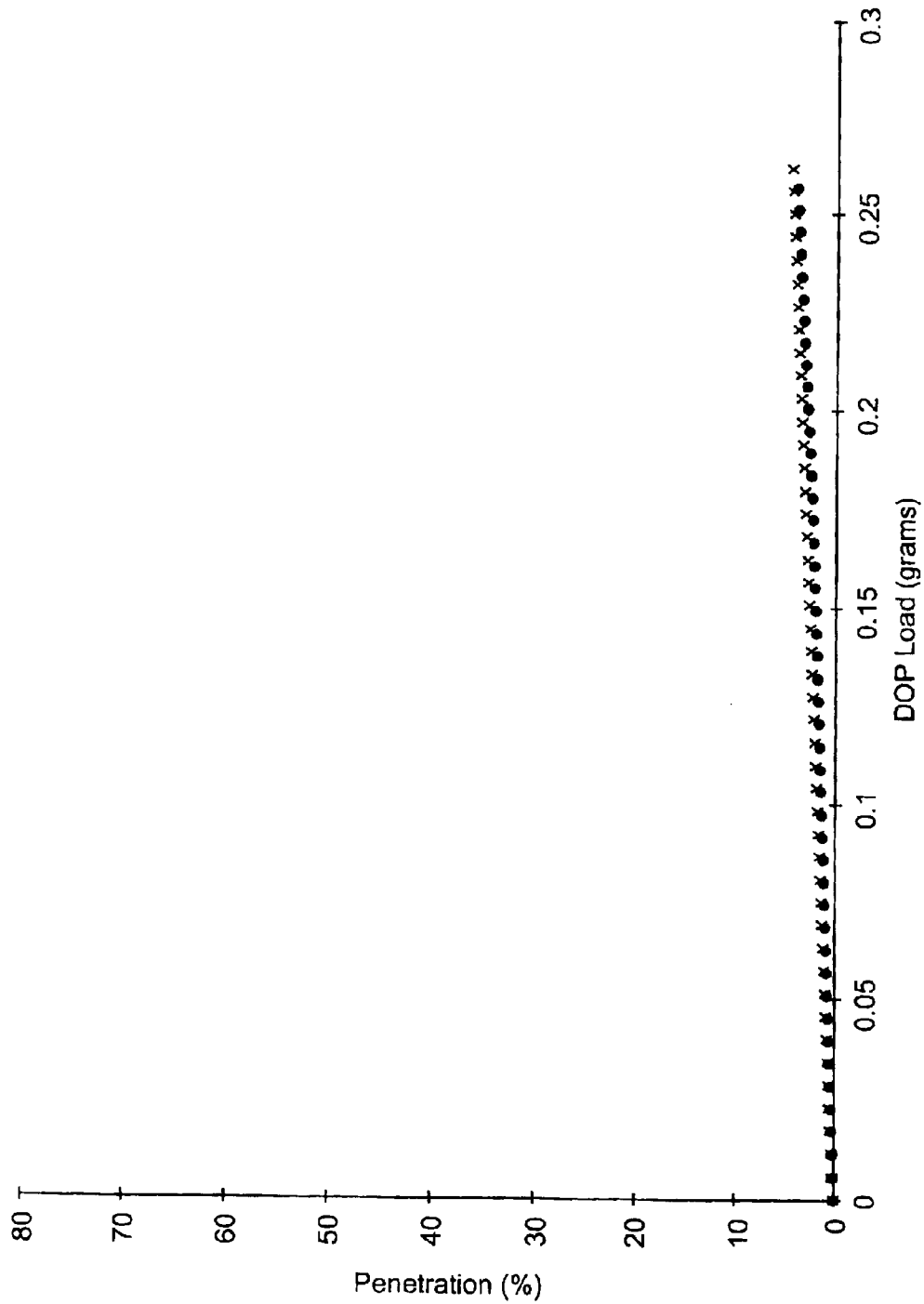


Fig. 1

U.S. Patent

Oct. 26, 2004

Sheet 2 of 3

US 6,808,551 B2

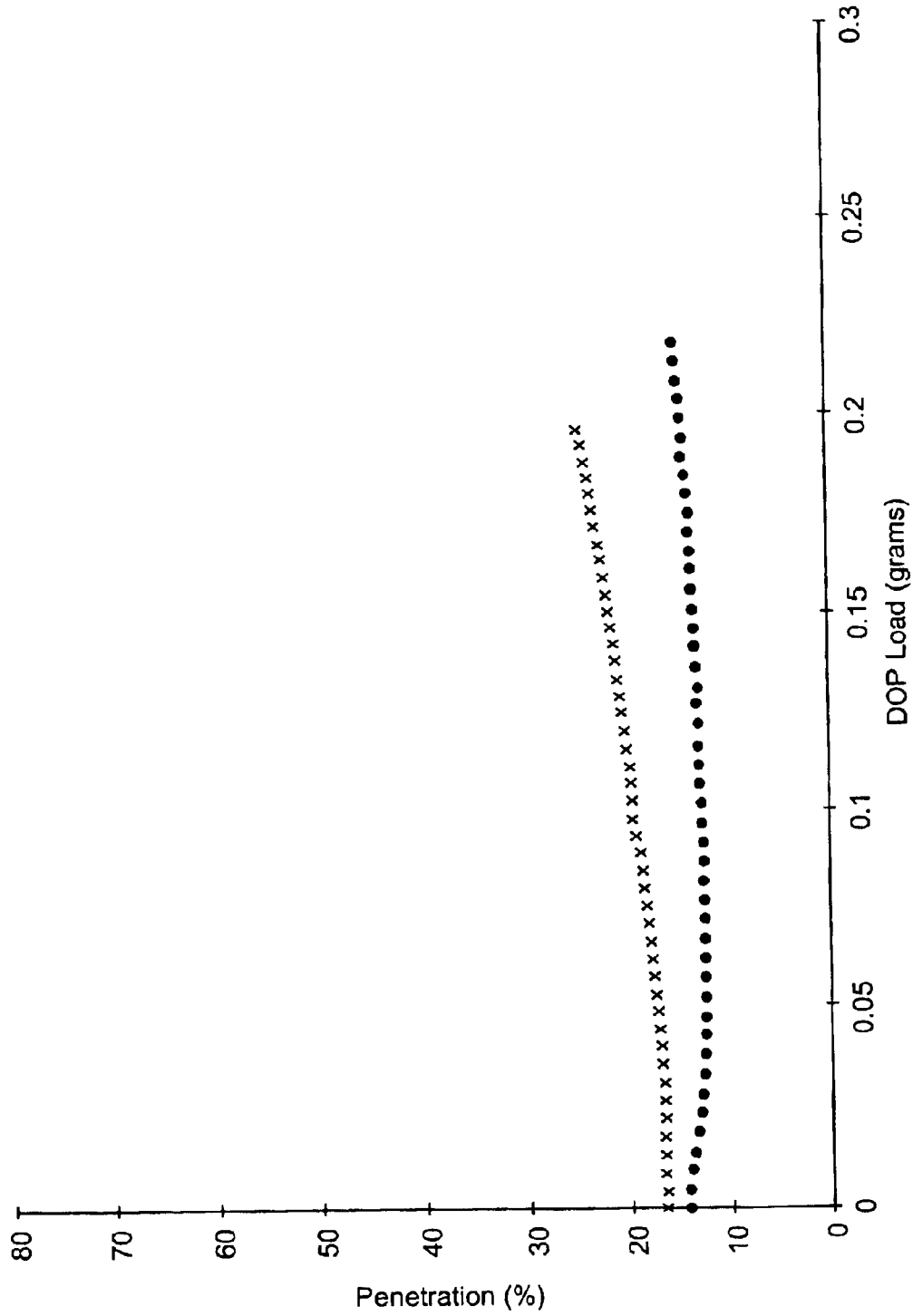


Fig. 2

U.S. Patent

Oct. 26, 2004

Sheet 3 of 3

US 6,808,551 B2

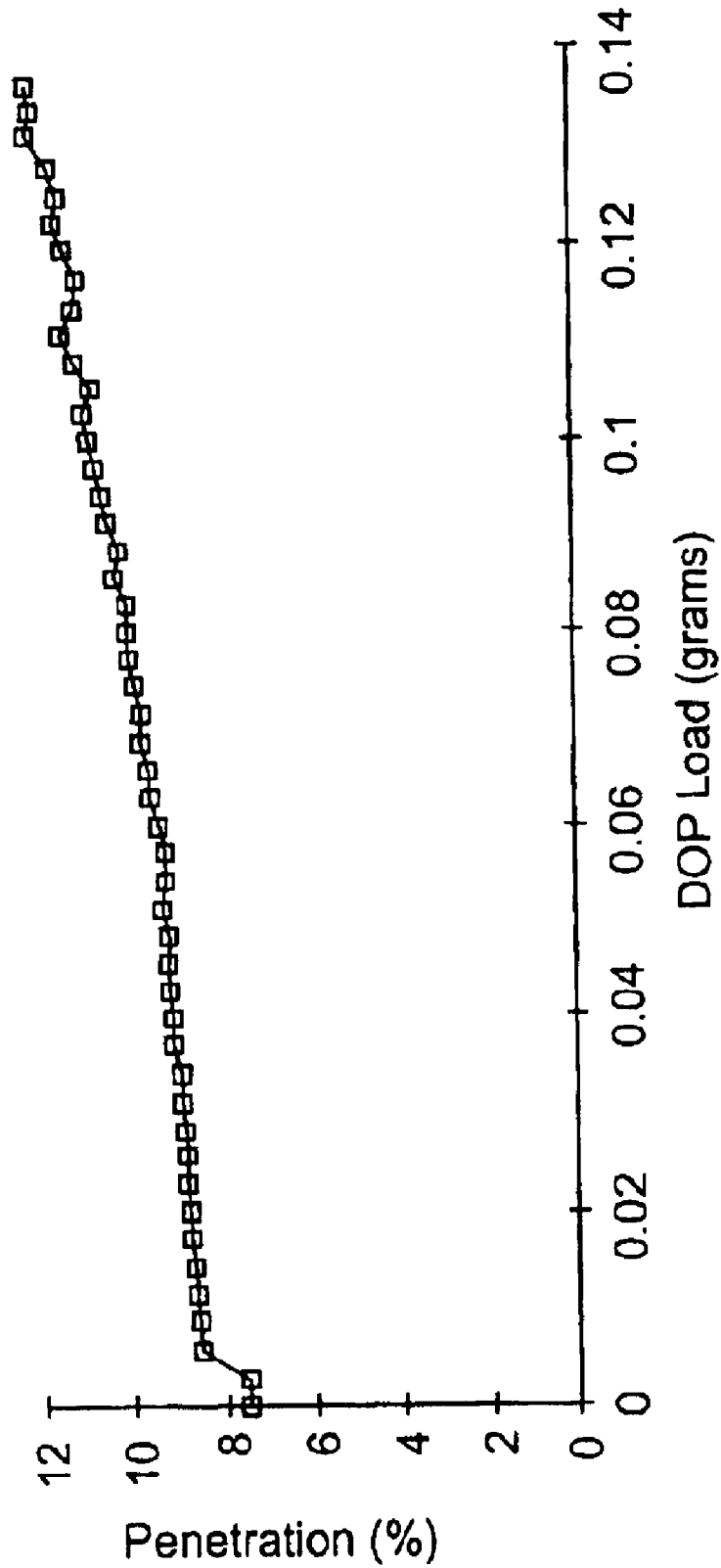


Fig. 3

US 6,808,551 B2

1

**METHOD OF USING FLUORINATED
ELECTRETS****CROSS-REFERENCE TO RELATED
APPLICATIONS**

This is a continuation of U.S. application Ser. No. 10/391,240, filed Mar. 18, 2003, now U.S. Pat. No. 6,660,210, which is a continuation of U.S. application Ser. No. 10/126,028, filed Apr. 19, 2002, now U.S. Pat. No. 6,562,112, which is a continuation of U.S. application Ser. No. 09/109,497, filed Jul. 2, 1998 now U.S. Pat. No. 6,432,175.

This invention relates to preparing fluorinated electrets.

BACKGROUND

The filtration properties of nonwoven polymeric fibrous webs can be improved by transforming the web into an electret, i.e., a dielectric material exhibiting a quasi-permanent electrical charge. Electrets are effective in enhancing particle capture in aerosol filters. Electrets are useful in a variety of devices including, e.g., air filters, face masks, and respirators, and as electrostatic elements in electro-acoustic devices such as microphones, headphones, and electrostatic recorders.

Electrets are currently produced by a variety of methods including direct current ("DC") corona charging (see, e.g., U.S. Pat. No. Re. 30,782 (van Turnhout)), and hydrocharging (see, e.g., U.S. Pat. No. 5,496,507 (Angadjivand et al.)), and can be improved by incorporating fluorochemicals into the melt used to produce the fibers of some electrets (see, e.g., U.S. Pat. No. 5,025,052 (Crater et al.)).

Many of the particles and contaminants with which electret filters come into contact interfere with the filtering capabilities of the webs. Liquid aerosols, for example, particularly oily aerosols, tend to cause electret filters to lose their electret enhanced filtering efficiency (see, e.g., U.S. Pat. No. 5,411,576 (Jones et al.)).

Numerous methods have been developed to compensate for loss of filtering efficiency. One method includes increasing the amount of the nonwoven polymeric web in the electret filter by adding layers of web or increasing the thickness of the electret filter. The additional web, however, increases the breathing resistance of the electret filter, adds weight and bulk to the electret filter, and increases the cost of the electret filter. Another method for improving an electret filter's resistance to oily aerosols includes forming the electret filter from resins that include melt processable fluorochemical additives such as fluorochemical oxazolidinones, fluorochemical piperazines, and perfluorinated alkanes. (See, e.g., U.S. Pat. No. 5,025,052 (Crater et al.)). The fluorochemicals should be melt processable, i.e., suffer substantially no degradation under the melt processing conditions used to form the microfibers that are used in the fibrous webs of some electrets. (See, e.g., WO 97/07272 (Minnesota Mining and Manufacturing)).

SUMMARY OF THE INVENTION

In one aspect, the invention features an electret that includes a surface modified polymeric article having surface fluorination produced by fluorinating a polymeric article.

In one embodiment, the article includes at least about 45 atomic % fluorine as detected by ESCA. In another embodiment, the article includes a $\text{CF}_3:\text{CF}_2$ ratio of at least about 0.25 as determined according to the Method for Determining $\text{CF}_3:\text{CF}_2$. In other embodiments, the article includes a $\text{CF}_3:\text{CF}_2$ ratio of at least about 0.45 as determined according to the Method for Determining $\text{CF}_3:\text{CF}_2$.

2

In one embodiment, the article has a Quality Factor of at least about 0.25/ mmH_2O , (preferably at least about 0.5/ mmH_2O , more preferably at least about 1/ mmH_2O).

In some embodiments, the article includes a nonwoven polymeric fibrous web. Examples of suitable fibers for the nonwoven polymeric fibrous web include polycarbonate, polyolefin, polyester, halogenated polyvinyl, polystyrene, and combinations thereof. Particularly useful fibers include polypropylene, poly-(4-methyl-1-pentene), and combinations thereof. In one embodiment, the article includes melt-blown microfibers.

In another aspect, the invention features an electret that includes a polymeric article having at least about 45 atomic % fluorine as detected by ESCA, and a $\text{CF}_3:\text{CF}_2$ ratio of at least about 0.45 as determined according to the Method for Determining $\text{CF}_3:\text{CF}_2$. In another embodiment, the electret includes at least about 50 atomic % fluorine as detected by ESCA, and a $\text{CF}_3:\text{CF}_2$ ratio of at least about 0.25 as determined according to the Method for Determining $\text{CF}_3:\text{CF}_2$.

In other aspects, the invention features a respirator that includes the above-described electrets. In still other aspects, the invention features a filter that includes the above-described electrets.

In one aspect, the invention features a method of making an electret that includes: (a) fluorinating a polymeric article to produce an article having surface fluorination; and (b) charging the fluorinated article in a manner sufficient to produce an electret. In one embodiment, the method includes charging the fluorinated article by contacting the fluorinated article with water in a manner sufficient to produce an electret, and drying the article. The method is useful for making the above-described electrets. In another embodiment, the method includes charging the fluorinated article by impinging jets of water or a stream of water droplets onto the fluorinated article at a pressure and for a period sufficient to produce an electret, and drying the article.

In other embodiments, the method includes fluorinating a polymeric article in the presence of an electrical discharge (e.g., an alternating current corona discharge at atmospheric pressure) to produce a fluorinated article. In one embodiment, the method includes fluorinating the polymeric article in an atmosphere that includes fluorine containing species selected from the group consisting of elemental fluorine, fluorocarbons, hydrofluorocarbons, fluorinated sulfur, fluorinated nitrogen and combinations thereof. Examples of suitable fluorine containing species include C_5F_{12} , C_2F_6 , CF_4 , hexafluoropropylene, SF_6 , NF_3 , and combinations thereof.

In other embodiments, the method includes fluorinating the polymeric article in an atmosphere that includes elemental fluorine.

In other embodiments, the method of making the electret includes: (A) fluorinating a nonwoven polymeric fibrous web (i) in an atmosphere that includes fluorine containing species and an inert gas, and (ii) in the presence of an electrical discharge to produce a web having surface fluorination; and (B) charging the fluorinated web in a manner sufficient to produce an electret.

In other aspects, the invention features a method of filtering that includes passing an aerosol through the above-described electrets to remove contaminants.

The fluorinated electrets of the invention exhibit a relatively high oily mist resistance relative to non-fluorinated electrets.

US 6,808,551 B2

3

GLOSSARY

In reference to the invention, these terms having the meanings set forth below: "electret" means a dielectric material exhibiting a quasi-permanent electrical charge. The term "quasi-permanent" means that the time constants characteristic for the decay of the charge are much longer than the time period over which the electret is used;

"surface modified" means that the chemical structure at the surface has been altered from its original state.

"surface fluorination" means the presence of fluorine atoms on a surface (e.g., the surface of an article);

"fluorine containing species" means molecules and moieties containing fluorine atoms including, e.g., fluorine atoms, elemental fluorine, and fluorine containing radicals;

"fluorinating" means placing fluorine atoms on the surface of an article by transferring fluorine containing species from a gaseous phase to the article by chemical reaction, sorption, condensation, or other suitable means;

"aerosol" means a gas that contains suspended particles in solid or liquid form; and

"contaminants" means particles and/or other substances that generally may not be considered to be particles (e.g., organic vapors).

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a plot of % DOP Penetration vs. DOP Load for Examples 36 and 37.

FIG. 2 is a plot of % DOP Penetration vs. DOP Load for Examples 38 and 39.

FIG. 3 is a plot of % DOP Penetration vs. DOP Load for Example 40.

DESCRIPTION OF PREFERRED EMBODIMENTS

The electret includes a surface modified polymeric article (e.g., a nonwoven polymeric fibrous web) produced by fluorinating a polymeric article. The electrets preferably have sufficient surface fluorination to provide oily mist resistance. One measure of oily mist resistance is how well the electret maintains its Quality Factor during challenge with an aerosol. The Quality Factor can be calculated from results obtained from the dioctylphthalate ("DOP") initial penetration test ("the DOP test"). The DOP test also provides a relative measure of the charge state of the filter. The DOP test procedure involves forcing DOP aerosol at a face velocity of 6.9 cm/second for a period of about 30 seconds through the sample, measuring the pressure drop across the sample (Pressure Drop measured in mmH₂O) with a differential manometer, and measuring the percent DOP penetration (DOPPen %). The Quality Factor (QF) (measured in 1/mmH₂O) can be calculated from these values according to the following formula:

$$QF[1/\text{mmH}_2\text{O}] = \frac{-\ln \frac{\text{DOPPenetration}(\%)}{100}}{\text{PressureDrop}[\text{mmH}_2\text{O}]}$$

The higher the Quality Factor at a given flow rate, the better the filtering performance of the electret.

Preferred electrets have a Quality Factor of at least about 0.25/mmH₂O, preferably at least about 0.5/mmH₂O, more preferably at least about 1.0/mmH₂O.

4

Electron spectroscopy for chemical analysis ("ESCA") (also known as X-ray photoelectron spectroscopy ("XPS")) provides one measure of surface fluorination. Preferably the surface of the electret exhibits at least about 45 atomic % fluorine, more preferably at least about 50 atomic % fluorine when analyzed by ESCA. ESCA analyzes the elemental composition of the outermost surface (i.e., approximately 10 to 50 Å) of a specimen. ESCA can be used to detect all elements in the periodic table except helium and hydrogen.

The electret also has a CF₃:CF₂ ratio at the surface of the electret of at least about 0.25, preferably at least about 0.45, and more preferably greater than 0.9, as determined according to the Method For Determining CF₃:CF₂ ratio set forth in the Example section below.

In one embodiment, the electrets include nonwoven polymeric fibrous webs that include fibers such as, e.g., melt-blown microfibers, staple fibers, fibrillated films, and combinations thereof. The fibers can be formed from resins. Preferably the resin is a thermoplastic nonconductive, i.e., having a resistivity of greater than 10¹⁴ ohm-cm, resin. The resin used to form the fibers should be substantially free of materials such as antistatic agents that could increase the electrical conductivity or otherwise interfere with the ability of the fibers to accept and hold electrostatic charges.

Examples of useful thermoplastic resins include polyolefins such as, e.g., polypropylene, polyethylene, poly-(4-methyl-1-pentene), and combinations thereof, halogenated vinyl polymers (e.g., polyvinyl chloride), polystyrene, polycarbonates, polyesters, and combinations thereof.

Additives can be blended with the resin including, e.g., pigment, UV stabilizers, antioxidants, and combinations thereof.

Meltblown microfibers can be prepared as described in Wente, Van A., "Superfine Thermoplastic Fibers," *Industrial Eng. Chemistry*, Vol. 48, pp. 1342-1346 and in Report No. 4364 of the Naval Research laboratories, published May 25, 1954, entitled, "Manufacture of Super Fine Organic Fibers," by Wente et al. Meltblown microfibers preferably have an effective fiber diameter in the range of less than 1 to 50 μm as calculated according to the method set forth in Davies, C. N., "The Separation of Airborne Dust and Particles," Institution of Mechanical Engineers, London, Proceedings 1B, 1952.

The presence of staple fibers provides a more lofty, less dense web than a web constructed solely of meltblown microfibers. Preferably the electret contains more than 70% by weight staple fibers. Webs containing staple fibers are disclosed in U.S. Pat. No. 4,118,531 (Hauser).

Electrets that include a nonwoven polymeric fibrous web preferably have a basis weight in the range of about 10 to 500 g/m², more preferably about 10 to 100 g/m². The thickness of the nonwoven polymeric fibrous web is preferably about 0.25 to 20 mm, more preferably about 0.5 to 2 mm.

The nonwoven polymeric webs of the electret can also include particulate matter as disclosed, for example, in U.S. Pat. Nos. 3,971,373, (Braun), 4,100,324 (Anderson), and 4,429,001 (Kolpin et al.).

Electret Preparation

The electrets can be prepared by fluorinating a polymeric article, optionally in the presence of a surface modifying electrical discharge, and charging the fluorinated article to produce an electret.

The fluorination process includes modifying the surface of the polymeric article to contain fluorine atoms by exposing the polymeric article to an atmosphere that includes

US 6,808,551 B2

5

fluorine containing species. The fluorination process can be performed at atmospheric pressure or under reduced pressure. The fluorination process is preferably performed in a controlled atmosphere to prevent contaminants from interfering with the addition of fluorine atoms to the surface of the article. The atmosphere should be substantially free of oxygen and other contaminants. Preferably the atmosphere contains less than 0.1% oxygen.

The fluorine containing species present in the atmosphere can be derived from fluorinated compounds that are gases at room temperature, become gases when heated, or are capable of being vaporized. Examples of useful sources of fluorine containing species include, fluorine atoms, elemental fluorine, fluorocarbons (e.g., C_5F_{12} , C_3F_6 , CF_4 , and hexafluoropropylene), hydrofluorocarbons (e.g., CF_3H), fluorinated sulfur (e.g., SF_6), fluorinated nitrogen (e.g., NF_3), fluorochemicals such as e.g., CF_3CF_3 and fluorochemicals available under the trade designation Fluorinert such as, e.g., Fluorinert FC-43 (commercially available from Minnesota Mining and Manufacturing Company, Minnesota), and combinations thereof.

The atmosphere of fluorine containing species can also include an inert diluent gas such as, e.g., helium, argon, nitrogen, and combinations thereof.

The electrical discharge applied during the fluorination process is capable of modifying the surface chemistry of the polymeric article when applied in the presence of a source of fluorine containing species. The electrical discharge is in the form of plasma, e.g., glow discharge plasma, corona plasma, silent discharge plasma (also referred to as dielectric barrier discharge plasma and alternating current ("AC") corona discharge), and hybrid plasma, e.g., glow discharge plasma at atmospheric pressure, and pseudo glow discharge. Preferably the plasma is an AC corona discharge plasma at atmospheric pressure. Examples of useful surface modifying electrical discharge processes are described in U.S. Pat. Nos. 5,244,780, 4,828,871, and 4,844,979.

Another fluorination process includes immersing a polymeric article into a liquid that is inert with respect to elemental fluorine, and bubbling elemental fluorine gas through the liquid to produce a surface fluorinated article. Examples of useful liquids that are inert with respect to fluorine include perhalogenated liquids, e.g., perfluorinated liquids such as Performance Fluid PF 5052 (commercially available from Minnesota Mining and Manufacturing Company). The elemental fluorine containing gas that is bubbled through the liquid can include an inert gas such as, e.g., nitrogen, argon, helium, and combinations thereof.

Charging the polymeric article to produce an electret can be accomplished using a variety of techniques, including, e.g., hydrocharging, i.e., contacting an article with water in a manner sufficient to impart a charge to the article, followed by drying the article, and DC corona charging. The charging process can be applied to one or more surfaces of the article.

One example of a useful hydrocharging process includes impinging jets of water or a stream of water droplets onto the article at a pressure and for a period sufficient to impart a filtration enhancing electret charge to the web, and then drying the article. The pressure necessary to optimize the filtration enhancing electret charge imparted to the article will vary depending on the type of sprayer used, the type of polymer from which the article is formed, the type and concentration of additives to the polymer, and the thickness and density of the article. Pressures in the range of about 10 to about 500 psi (69 to 3450 kPa) are suitable. An example of a suitable method of hydrocharging is described in U.S. Pat. No. 5,496,507 (Angadjivand et al.).

6

The jets of water or stream of water droplets can be provided by any suitable spray device. One example of a useful spray device is the apparatus used for hydraulically entangling fibers.

Examples of suitable DC corona discharge processes are described in U.S. Pat. No. Re. 30,782 (van Turnhout), U.S. Pat. No. Re. 31,285 (van Turnhout), U.S. Pat. No. Re. 32,171 (van Turnhout), U.S. Pat. No. 4,375,718 (Wadsworth et al.), U.S. Pat. No. 5,401,446 (Wadsworth et al.), U.S. Pat. No. 4,588,537 (Klasse et al.), and U.S. Pat. No. 4,592,815 (Nakao).

The fluorinated electrets formed by the methods described herein are suitable for use as, e.g., electrostatic elements in electro-acoustic devices such as microphones, headphones and speakers, fluid filters, dust particle control devices in, e.g., high voltage electrostatic generators, electrostatic recorders, respirators (e.g., prefilters, canisters and replaceable cartridges), heating, ventilation, air conditioning, and face masks.

The invention will now be described further by way of the following examples.

EXAMPLES

Test Procedures

Test procedures used in the examples include the following.

Method for Determining $CF_3:CF_2$

ESCA data was collected on a PHI 5100 ESCA system (Physical Electronics, Eden Prairie, Minn.) using a non-monochromatic $MgK\alpha$ x-ray source and a 45 degree electron takeoff angle with respect to the surface. The carbon (1s) spectra were peak fit using a nonlinear least-squares routine supplied by PHI (Physical Electronics, Eden Prairie, Minn.). This routine used a linear background subtraction, and a gaussian peak shape for the component peaks. The spectra were referenced to the hydrocarbon peak at 285.0 eV. The CF_3 and CF_2 components were identified as the peaks located at about 294 eV and 292 eV respectively (according to the procedure described in Strobel et al., J. Polymer Sci. A: Polymer Chemistry, Vol. 25, pp.1295-1307 (1987)). The $CF_3:CF_2$ ratio represent the ratio of the peak areas of the CF_3 and CF_2 components.

Initial Dioctylphthalate Penetration (DOP) and Pressure Drop Test Procedure

Initial DOP penetration is determined by forcing 0.3 micrometer diameter dioctyl phthalate (DOP) particles at a concentration of between 70 and 140 mg/m^3 (generated using a TSI No. 212 sprayer with four orifices and 30 psi clean air) through a sample of filter media which is 4.5 inches in diameter at a rate of 42.5 L/min (a face velocity of 6.9 centimeters per second). The sample is exposed to the DOP aerosol for 30 seconds until the readings stabilize. The penetration is measured with an optical scattering chamber, Percent Penetration Meter Model TPA-8F available from Air Techniques Inc.

Pressure drop across the sample is measured at a flow rate of 42.5 L/min (a face velocity of 6.9 cm/sec) using an electronic manometer. Pressure drop is reported in mm of water ("mm H_2O ").

DOP penetration and pressure drop are used to calculate the quality factor "QF" from the natural log (ln) of the DOP penetration by the following formula:

US 6,808,551 B2

7

$$QF[1/\text{mmH}_2\text{O}] = \frac{-\text{Ln} \frac{\text{DOP Penetration}(\%)}{100}}{\text{Pressure Drop} [\text{mmH}_2\text{O}]}$$

A higher initial QF indicates better initial filtration performance. A decreased QF effectively correlates with decreased filtration performance.

DOP Loading Test

DOP loading is determined using the same test equipment used in the DOP penetration and pressure drop tests. The test sample is weighed and then exposed to the DOP aerosol for at least 45 min to provide a minimum exposure of at least about 130 mg. DOP penetration and pressure drop are measured throughout the test at least as frequently as once per minute. The mass of DOP collected is calculated for each measurement interval from the measured penetration, mass of the filter web, and total mass of DOP collected on the filter web during exposure ("DOP Load").

Corona Fluorination

Example 1

A blown polypropylene microfiber web prepared from Exxon 3505G polypropylene resin (Exxon Corp.) and having an effective fiber diameter of 7.5 μm and a basis weight of 62 g/m² was prepared as described in Wentz, Van A., "Superfine Thermoplastic Fibers," *Industrial Eng. Chemistry*, Vol. 48, pp. 1342-1346.

The blown microfiber web was then AC corona fluorinated in a 1% by volume C₂F₆ in helium atmosphere at a corona energy of 34 J/cm², which corresponded to a corona power of 2000W at a substrate speed of 1 m/min. The AC corona fluorination treatment was performed in an AC corona system that included the so-called "double-dielectric" electrode configuration with a ground roll consisting of 40 cm diameter nickel-plated aluminum roll covered with 1.5 mm of poly(ethylene terephthalate) and maintained at a temperature of 23° C. using recirculating, pressurized water. The powered electrodes consisted of 15 individual ceramic-covered electrodes (available from Sherman treaters Ltd., Thame, United Kingdom) each with a 15 mm square cross-section and an active length of 35 cm. The electrodes were connected to a model RS48-B (4 kW) variable-frequency power supply (available from ENI Power Systems Inc., Rochester, N.Y.). The net power dissipated in the AC corona was measured with a directional power meter incorporated into the ENI supply. The frequency of the output power was manually adjusted to about 16 kHz to obtain optimal impedance matching (minimum reflected power).

The AC corona system was enclosed within a controlled environment. Prior to treatment, the atmosphere surrounding the AC corona treatment system was purged with helium, and then continually flushed with 100 liters/min of 1% by volume C₂F₆ in helium, which was introduced near the electrodes.

The microfiber web was taped onto a carrier film of 0.05 mm thick bi-axially-oriented polypropylene (BOPP), and then placed on the ground roll such that the carrier film was in contact with the ground roll, causing one side of the blown microfiber web to be exposed to the discharge. After treatment, the blown microfiber web was flipped over, retaped to the carrier film, and AC corona treated a second time under the same conditions as the first treatment to expose the other side of the blown microfiber web to the discharge.

8

Example 2

A G100 Filtrete fibrillated film web (available from Minnesota Mining and Manufacturing), having a basis weight of 100 g/m², was corona fluorinated following the method described in Example 1, with the exception that the ground roll was maintained at a temperature of 25° C.

Example 3

A polyethylene meltblown microfiber web, prepared from Aspun PE-6806 polyethylene resin (DOW Chemical Company, Michigan) and having a basis weight of 107 g/m², was corona fluorinated following the method described in Example 2.

Example 4

A polyester staple fiber web (available from Rogers Corporation), having a basis weight of 200 g/m², was corona fluorinated following the method described in Example 2.

Example 5

A poly-4-methyl-1-pentene meltblown microfiber web prepared from TPX MX-007 poly-4methyl-1-pentene resin (Mitsui), and having a basis weight of 50 g/m² and an effective fiber diameter of 8.1 μm , was corona fluorinated following the method described in Example 2.

Examples 6-9

Examples 6-9 were prepared following the procedure in Example 1 except that the source of containing species was as follows: 1% CF₄ (Example 6), and 0.1% hexafluoropropylene (Example 7), 0.1% C₅F₁₂ (Example 8), and 1.0% C₅F₁₂ (Example 9).

The surface chemistry of each of the sample webs of Examples 1-9 was determined by ESCA analysis using a PHI 5100 ESCA system. The CF₃:CF₂ ratio was determined for each of the samples of Examples 1-9 from the ESCA data according to the above-described method. The results are reported in atomic % in Table I.

TABLE I

Example	Carbon	Nitrogen	Oxygen	Fluorine	CF ₃ :CF ₂
1	43		5.7	51	1.09
2	44		6.2	50	1.37
3	49	0.2	8.2	42	1.10
4	42	0.5	7.8	49	0.99
5	44	0.0	2.9	53	1.19
6	41		3.5	55	0.86
7	41		2.7	56	0.97
8	42		6.4	52	0.91
9	43		5.2	51	0.89

Hydrocharging

Example 10

A fluorinated polypropylene blown microfiber web prepared as described above in Example 1, was passed over a vacuum slot at a rate of 5 cm/sec (centimeters/second) while deionized water was sprayed onto the web at a hydrostatic pressure of about 90 psi from a pair of Spraying Systems Teejet 9501 sprayer nozzles mounted 10 cm apart and centered 7 cm above the vacuum slot. The sample was then inverted and passed through the deionized water spray a second time such that both sides of the web were sprayed

US 6,808,551 B2

9

with water. The deionized water spray was then removed and the web was again passed over the vacuum slot to remove excess water. The web was then hung to dry at ambient conditions.

Example 11

A fluorinated poly-4-methyl-1-pentene meltblown microfiber web prepared according to Example 5 was charged following the procedure of Example 10.

Examples 10A–11A

Examples 10A–11A were prepared following the procedures of Example 10 and 11 respectively, with the exception that, after corona fluorination and prior to hydrocharging, each of the fluorinated webs of Examples 10A–11A were subjected to an anneal at 140° C. (300° F.) for about 10 minutes.

Examples 13, 15, 16, 18 and 20

Examples 13, 15, 16, 18 and 20 were charged following the procedure of Example 10, with the exception that the fluorinated polymeric fibrous webs used in each of Examples 13, 15, 16, 18 and 20 were as follows: a fluorinated polyethylene microfiber web prepared according to Example 3 above (Example 13); a fluorinated polyester staple fiber web prepared according to Example 4 (Example 15); a fluorinated G100 Filtrete fibrillated film web prepared according to Example 2 (Example 16); a fluorinated polypropylene needle punched web (12 denier/fiber fibers of Exxon 3505 polypropylene resin), having a basis weight of about 200 g/m², and having been corona fluorinated following the method described in Example 1 (Example 18); and a polypropylene melt blown fine fiber web, having a basis weight of 46 g/m² and an effective fiber diameter of 3.7 μm, and having been corona fluorinated following the method described in Example 1 with the exception that 0.2% C₅F₁₂ was used instead of 1% C₂F₆ (Example 20).

DC Corona Charging

Example 12

The fluorinated polyethylene meltblown microfiber web of Example 3 was charged using a DC corona discharge as follows. The fluorinated web was placed in contact with an aluminum ground plane, and then passed under an electrically positive DC corona source, in air, at a rate of about 1.2 meters/min, while maintaining a current to ground plane of about 0.01 mA/cm of corona source length. The distance from corona source to ground was about 4 cm.

Examples 14, 17, 19

Examples 14, 17 and 19 were charged following the procedure of Example 12, with the exception that the fluorinated polymeric fibrous webs for each of Examples 14, 17 and 19 were as follows: a fluorinated polyester staple fiber web prepared following the procedure of Example 4 (Example 14); a fluorinated polypropylene needle punched web (12 denier/fiber fibers made from Exxon 3505 polypropylene resin), having a basis weight of about 200 g/m², and having been corona fluorinated following the method described in Example 1 (Example 17); and a fluorinated polypropylene meltblown fine fiber web, having a basis weight of 46 g/m² and an effective fiber diameter of 3.7 μm, and having been corona fluorinated following the method described in Example 1 with the exception that 0.2% C₅F₁₂ was used instead of 1% C₂F₆ (Example 19).

10

Examples 21–35

Examples 21–35 were prepared by fluorinating polypropylene blown micro fiber webs following the procedure of Example 1, with the exception that the source of fluorine for each of Examples 21–35 was as follows: 1% CF₄ (Examples 21–23), 1% C₂F₆ (Examples 24–26), 0.1% hexafluoropropylene (Examples 27–29), 0.1% C₅F₁₂ (Examples 30–32), and 1.0% C₅F₁₂ (Examples 33–35).

The fluorinated webs of Examples 23, 26, 29, 32, and 35 were then charged following the hydrocharging process described above in Example 10.

The fluorinated webs of Examples 22, 25, 28, 31 and 34 were then charged following the DC corona charging process described above in Example 12.

% DOP penetration (“% DOP PEN”), Pressure Drop (mmH₂O), and the Quality Factor (“QF”) for each of the electrets of Examples 10–35 were determined according to the above-described Initial DOP Penetration and Pressure Drop Test Procedure. The results are summarized in Table II.

TABLE II

EXAMPLE	% DOP PEN	PRESSURE DROP	QF
10	0.119	3.65	1.84
10A	0.140	3.21	2.05
11	2.45	1.46	2.54
11A	0.778	1.60	3.04
12	56.1	1.14	0.51
13	38.1	1.15	0.84
14	78.3	0.38	0.64
15	65.6	0.41	1.03
16	27.3	0.40	3.25
17	70.4	0.19	1.85
18	37.6	0.19	5.15
19	0.81	10.58	0.46
20	0.006	11.3	0.86
21	55.6	2.83	0.21
22	15.0	3.28	0.58
23	0.288	3.09	1.89
24	54.1	3.05	0.20
25	14.3	3.32	0.59
26	0.243	3.08	1.95
27	59.0	2.81	0.19
28	16.2	2.80	0.65
29	0.276	2.90	2.03
30	52.5	3.15	0.20
31	14.0	3.11	0.63
32	0.250	2.99	2.00
33	45.3	3.10	0.26
34	14.9	2.93	0.65
35	0.244	3.14	1.92

Example 36–39

Four fluorinated, polypropylene microfiber webs were prepared according to Example 1 with the exception that the source of fluorine containing species was as follows: 0.1% hexafluoropropylene (“HFP”) (Examples 36 and 38) and 0.1% C₅F₁₂ (Example 37 and 39).

Examples 36 and 37 further included charging the fluorinated polypropylene webs following the hydrocharging charging procedure of Example 10.

Examples 38 and 39 further included charging the fluorinated polypropylene webs following the DC corona charging procedure of Example 12.

Examples 36–39 were subjected to the above-described DOP Loading Test. The % DOP Penetration versus DOP loading (the amount of DOP collected on the web in grams) for each of Examples 36–39 was measured according to the above-described DOP Loading Test Procedure. The result-

US 6,808,551 B2

11

ing data are plotted as % DOP penetration versus DOP load (grams) in FIGS. 1 and 2 as follows: Examples 36 and 37 (indicated with x's and solid circles respectively) (FIG. 1), and Examples 38 and 39 (indicated with x's and solid circles respectively) (FIG. 2).

Example 40

A 7 in. by 7 in. sample of polypropylene microfiber web having a basis weight of 61 g/m² was placed under a nitrogen atmosphere. A gaseous mixture of 5% by volume elemental fluorine diluted in nitrogen was passed through the polypropylene microfiber web at a rate of 1.0 l/min for 10 minutes. The fluorine concentration was then increased to 10% by volume diluted in nitrogen and passed through the web at a rate of 1.0 l/min for an additional 20 minutes.

The sample was then analyzed by ESCA and determined to have 62 atomic % fluorine and a CF₃:CF₂ ratio of 0.59, as determined according to the above-described Method for Determining CF₃:CF₂.

The sample was then charged using a DC corona discharge as described above in Example 12, and subjected to the above-described DOP Loading Test. The resulting data are plotted as % DOP Penetration versus DOP Load (grams) in FIG. 3.

Example 41

A polypropylene blown microfiber web, having a basis weight of 20 g/m² and a web width of 15 cm, was vacuum glow-discharge treated in a C₅F₁₂ environment. The glow-discharge treatment was performed in a vacuum chamber. The vacuum chamber contained a roll-to-roll glow discharge system consisting of an unwind roller, glow discharge electrodes, and a windup roller for the continuous treatment of the blown microfiber web. Two stainless steel electrodes were in the parallel plate configuration, each electrode was 20 cm wide and 33 cm long and they were separated by a gap of 2.5 cm. The top electrode was grounded and the bottom electrode was powered by a 13.56 MHz rf generator (Plasma-Therm). The web traveled between the two electrodes and in contact with the top, grounded electrode so that one side of the web was exposed to the discharge.

After loading the roll of blown microfiber web onto the unwind roller under C₅F₁₂ vapor at a pressure of 0.1 Torr. The blown microfiber web was advanced through the electrodes at a speed of 17 cm/min to achieve an exposure time to the plasma of 2 minutes. The discharge power was 50W. After the first side was treated, the chamber was vented and the web roll replaced onto the unwind roller to allow the other side of the web to be treated. The treatment of the second side of the web occurred under the same conditions as the first side. After the fluorination, Example 41 was DC-corona charged following the process described above in Example 12.

% DOP Penetration (" % DOP PEN") for Example 41 was determined according to the above-described Initial DOP Penetration and Pressure Drop Test Procedure. The results are summarized in Table III.

12

TABLE III

Loading Time (min)	% DOP Penetration Example 14
0.5	28
10	28

Other embodiments are within the following claims. Although the electret has been described with reference to nonwoven polymeric fibrous webs, the electret can be a variety of polymeric articles including, e.g., those polymeric articles described in U.S. patent application Ser. No. 09/106,506, entitled, "Structured Surface Filter Media," (Insley et al.), filed on Jun. 18, 1998.

All of the patents and patent applications cited above are incorporated by reference into this document in total.

What is claimed is:

1. A method of filtering contaminants, said method comprising:

passing an aerosol through a plasma surface modified nonwoven polymeric web electret to remove contaminants from the aerosol,

the nonwoven polymeric web comprising plasma surface fluorination, the electret, when tested according to the Initial DOP Penetration Test and the DOP Loading Test prior to contact with the aerosol, exhibiting a DOP penetration of less than 20% for a DOP load from 0.05 grams to 0.2 grams.

2. The method of claim 1 wherein the electret is part of a dust particle control device.

3. The method of claim 1, wherein the electret exhibits a DOP penetration of less than 15% for a DOP load of from 0.05 grams to 0.2 grams prior to contact with the aerosol.

4. The method of claim 1, wherein the electret exhibits a DOP penetration of less than 10% for a DOP load from 0.05 grams to 0.2 grams prior to contact with the aerosol.

5. The method of claim 1, wherein the electret exhibits a DOP penetration of no greater than 5% for a DOP load from 0.05 grams to 0.2 grams prior to contact with the aerosol.

6. The method of claim 1, wherein the electret exhibits a DOP penetration of less than 10% for a DOP load of from 0.02 grams to 0.08 grams prior to contact with the aerosol.

7. The method of claim 1, wherein the web comprises at least 45 atomic % fluorine as detected by ESCA.

8. The method of claim 1, wherein the web comprises a CF₃:CF₂ ratio of at least 0.45 as determined according to the Method of Determining CF₃:CF₂.

9. The method of claim 1, wherein the web comprises at least 45 atomic % fluorine as detected by ESCA and a CF₃:CF₂ ratio of at least 0.45 as determined according to the Method of Determining CF₃:CF₂.

10. The method of claim 1, wherein the web comprises a surface fluorination of at least 50 atomic % fluorine as detected by ESCA.

11. The method of claim 1, wherein the web comprises at least 50 atomic % fluorine as detected by ESCA and a CF₃:CF₂ ratio of at least 0.25 as determined according to the Method for Determining CF₃:CF₂.

12. The method of claim 1, wherein the web comprises at least 50 atomic % fluorine as detected by ESCA and a CF₃:CF₂ ratio of at least 0.45 as determined according to the Method for Determining CF₃:CF₂.

13. The method of claim 1, wherein the web comprises a CF₃:CF₂ ratio of at least 0.9.

14. The method of claim 1, wherein the web comprises at least 50 atomic % fluorine as detected by ESCA and a

US 6,808,551 B2

13

CF₃:CF₂ ratio of at least 0.9 as determined according to the Method for Determining CF₃:CF₂.

15. The method of claim 1, wherein the electret exhibits a Quality Factor of at least 0.5/mmH₂O prior to contact with the aerosol.

16. The method of claim 1, wherein the electret exhibits a Quality Factor of at least 2/mmH₂O prior to contact with the aerosol.

17. The method of claim 1, wherein the web comprises fibers selected from the group consisting of polycarbonate, polyolefin, polyester, halogenated polyvinyl, polystyrene, or a combination thereof.

18. The method of claim 1, wherein the web comprises fibers selected from the group consisting of polypropylene, poly-(4-methyl-1-pentene), or a combination thereof.

19. The method of claim 1, wherein the web comprises meltblown microfibers.

20. The method of claim 19, wherein the microfibers comprise polypropylene.

21. The method of claim 1, wherein the web has a basis weight of from 10 to 100 g/m².

22. A method of filtering contaminants, said method comprising:

passing an aerosol through an electret to remove contaminants from the aerosol,

the electret comprising a nonwoven polymeric web comprising at least about 45 atomic % fluorine as detected by ESCA and a CF₃:CF₂ ratio of at least about 0.45 as determined according to the Method of Determining CF₃:CF₂,

the electret having a Quality Factor of at least about 0.25/mmH₂O prior to contact with the aerosol.

23. The method of claim 22, wherein the electret has a Quality Factor of at least about 0.5/mmH₂O prior to contact with the aerosol.

24. The method of claim 22, wherein the electret has a Quality Factor of at least about 1/mmH₂O prior to contact with the aerosol.

25. The method of claim 22, wherein the nonwoven polymeric web comprises fibers selected from the group consisting of polycarbonate, polyolefin, polyester, halogenated polyvinyl, polystyrene, or a combination thereof.

26. The method of claim 22, wherein the nonwoven polymeric web comprises fibers selected from the group consisting of polypropylene, poly-(4-methyl-1-pentene), or a combination thereof.

14

27. The method of claim 22, wherein the nonwoven polymeric web comprises meltblown microfibers.

28. A method of filtering contaminants, said method comprising:

passing an aerosol through an electret to remove contaminants from the aerosol,

the electret comprising a nonwoven polymeric web comprising at least about 50 atomic % fluorine as detected by ESCA and a CF₃:CF₂ ratio of at least about 0.25 as determined according to the Method for Determining CF₃:CF₂,

the electret having a quality factor of at least about 0.25/mmH₂O prior to contact with the aerosol.

29. A method of filtering contaminants, said method comprising:

passing an aerosol through an electret to remove contaminants from the aerosol,

the electret comprising a nonwoven polymeric web comprising microfibers, the web having surface fluorination that comprises CF₃ and CF₂ at a CF₃:CF₂ ratio of at least 0.45 as determined according to the Method for Determining CF₃:CF₂,

the electret having a quality factor of at least about 0.25/mmH₂O prior to contact with the aerosol.

30. The method of claim 29, wherein the electret has a Quality Factor of at least about 1.0/mmH₂O.

31. The method of claim 29, wherein the web has a surface fluorination of at least about 45 atomic % fluorine as detected by ESCA.

32. The method of claim 29, wherein the CF₃:CF₂ ratio is at least 0.9.

33. The method of claim 29, wherein the microfibers are melt-blown microfibers that have an effective fiber diameter of 1 to 50 μm.

34. The method of claim 29, wherein the microfibers comprise polyolefin.

35. The method of claim 29, wherein the microfibers comprise polypropylene.

36. The method of claim 29, wherein the nonwoven web has a basis weight of 10 to 100 g/m².

37. The method of claim 29, wherein the nonwoven web has a thickness of 0.25 to 20 mm.

* * * * *

UNITED STATES PATENT AND TRADEMARK OFFICE
CERTIFICATE OF CORRECTION

PATENT NO. : 6,808,551 B2
DATED : October 26, 2004
INVENTOR(S) : Jones, Marvin E.

Page 1 of 1

It is certified that error appears in the above-identified patent and that said Letters Patent is hereby corrected as shown below:

Column 4,

Line 18, after "thereof" insert -- . --.

Column 5,

Line 17, delete "CF₃CF₃" and insert -- CF₃OCF₃ --, therefor.

Line 28, delete "," and insert -- . --, therefor.

Line 37, delete "4,844 979" and insert -- 4,844,979 --, therefor.

Column 6,

Line 66, delete "(In)" and insert -- (Ln) --, therefor.

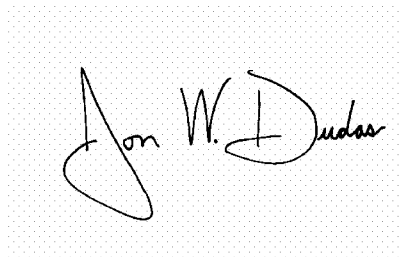
Column 8,

Line 24, delete "poly-4methyl-1-pentene" and insert -- poly-4-methyl-1-pentene --, therefor.

Line 32, insert -- fluorine -- before "containing".

Signed and Sealed this

Fifteenth Day of February, 2005

A handwritten signature in black ink on a light gray dotted background. The signature is written in a cursive style and reads "Jon W. Dudas".

JON W. DUDAS

Director of the United States Patent and Trademark Office